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                 IMSPRODUCT reloaded with enhancements
NEWS 13 FEB 29
                 WPINDEX/WPIDS/WPIX enhanced with ECLA and current
                 U.S. National Patent Classification
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                 IPC display formats
NEWS 15 MAR 31
                 CAS REGISTRY enhanced with additional experimental
                 spectra
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                 CA/CAplus and CASREACT patent number format for U.S.
                 applications updated
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                 LPCI now available as a replacement to LDPCI
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                 EMBASE, EMBAL, and LEMBASE reloaded with enhancements
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        APR 28
                 IMSRESEARCH reloaded with enhancements
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                                                              SESSION
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                                                      0.21
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=> s (slurry or particle(1a)form)(3a)(polymeri?)
         11468 (SLURRY OR PARTICLE(1A) FORM) (3A) (POLYMERI?)
=> s (olefin? or ethylene or ethene)(s)((loop or circular)(3a)reactor#)
          1448 (OLEFIN? OR ETHYLENE OR ETHENE)(S)((LOOP OR CIRCULAR)(3A) REACTO
L2
              R#)
\Rightarrow s 11 and 12
          734 L1 AND L2
T.3
=> s ((loop or circular)(3a)reactor#)(s)(solids(3a)(concentrat? or content or
level))
           191 ((LOOP OR CIRCULAR)(3A) REACTOR#)(S)(SOLIDS(3A)(CONCENTRAT? OR
L4
              CONTENT OR LEVEL))
\Rightarrow s 13 and 14
           81 L3 AND L4
L5
=> s ((loop or circular)(3a)reactor#) and ((ethylene or ethene)(6a)(concentrat? or
(weight or mol##)(2a)percent?))
          925 ((LOOP OR CIRCULAR)(3A) REACTOR#) AND ((ETHYLENE OR ETHENE)(6A)(
              CONCENTRAT? OR (WEIGHT OR MOL##)(2A) PERCENT?))
=> s 15 and 16
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=> d 17 1-53 ibib abs

L7 ANSWER 1 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2008:44974 USPATFULL

Process And Apparatus For Producing Olefin Polymers TITLE:

INVENTOR(S): Vuorikari, Marianna, Hamari, FINLAND

> Korhonen, Esa, Porvoo, FINLAND Andtsjo, Henrik, Porvoo, FINLAND Zitting, Samuli, Tuusula, FINLAND

PATENT ASSIGNEE(S): Borealis Technology OY, Porvoo, FINLAND, FI-06101

(non-U.S. corporation)

KIND DATE NUMBER _____ US 2008039597 A1 20080214 US 2005-578138 A1 20050429 WO 2005-FI202 20050429 PATENT INFORMATION: APPLICATION INFO.: (11)20050429 20061219 PCT 371 date

> NUMBER DATE _____

PRIORITY INFORMATION: EP 2004-396032 20040429

DOCUMENT TYPE: Utility APPLICATION FILE SEGMENT:

LEGAL REPRESENTATIVE: BIRCH STEWART KOLASCH & BIRCH, PO BOX 747, FALLS

CHURCH, VA, 22040-0747, US

NUMBER OF CLAIMS: 24

EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Page(s)

LINE COUNT: 576

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention concerns a process and an apparatus for continuous polymerisation of olefin monomers. In particular, the present invention concerns a process and an apparatus for continuous polymerisation olefin monomers like ethylene and other monomers, wherein an olefin monomer is polymerised in slurry phase in an inert hydrocarbon diluent in at least one loop reactor. According to the invention, a polymer slurry is continuously withdrawn from the loop reactor and concentrated. The concentrated slurry is conducted to a flash unit in order to remove the remaining fluid phase, and gas obtained is compressed in a flash gas compressor before

it is being fed to a distillation section. By means of the present invention it is possible reduce the size of the flash gas compressor and the capacity of the distillation sections. This significantly reduces investment cost for a continuously operated polymerization apparatus.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 2 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2007:314678 USPATFULL

TITLE: Continuous Slurry Polymerization

Process and Apparatus

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

KIND DATE NUMBER

PATENT INFORMATION: US 2007274873 A1 20071129 APPLICATION INFO.: US 2007-832156 A1 20070801 (11)

RELATED APPLN. INFO.:

Division of Ser. No. US 2002-85809, filed on 28 Feb 2002, GRANTED, Pat. No. US 7268194 Continuation-in-part of Ser. No. US 2002-79226, filed on 19 Feb 2002, GRANTED, Pat. No. US 6833415 Continuation-in-part of Ser. No. US 2001-955729, filed on 19 Sep 2001, PENDING Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, GRANTED, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, GRANTED, Pat. No. US 6204344 Continuation-in-part of Ser. No. US

1998-80412, filed on 18 May 1998, ABANDONED

Continuation-in-part of Ser. No. US 1998-81392, filed

on 18 May 1998, GRANTED, Pat. No. US 6281300

DATE NUMBER _____

PRIORITY INFORMATION:

US 1998-78859P 19980320 (60) US 1998-78859P 19980320 (60)

DOCUMENT TYPE: FILE SEGMENT:

Utility APPLICATION

LEGAL REPRESENTATIVE: EXXONMOBIL CHEMICAL COMPANY, 5200 BAYWAY DRIVE, P.O.

BOX 2149, BAYTOWN, TX, 77522-2149, US

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1

6 Drawing Page(s) NUMBER OF DRAWINGS:

LINE COUNT: 1731

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 3 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2007:291320 USPATFULL

TITLE: Polymerization Reactors with a By-Pass Line

INVENTOR(S): Fouarqe, Louis, Dilbeek, BELGIUM Davidts, Sandra, Battice, BELGIUM

		NUMBER	KIND	DATE	
PATENT INFORMATION:	US	2007255019	A1	20071101	
APPLICATION INFO.:	US	2005-631374	A1	20050628	(11)
	WO	2005-EP53025		20050628	

20061229 PCT 371 date

NUMBER DATE ______ PRIORITY INFORMATION: EP 2004-103110 20040701

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: FINA TECHNOLOGY INC, PO BOX 674412, HOUSTON, TX,

77267-4412, US

21 NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1-15

NUMBER OF DRAWINGS: 2 Drawing Page(s)
353

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention discloses a slurry loop reactor

having at least two loops (1, 2) and comprising a by-pass line (11)

connecting two points (12, 13) of the same loop

reactor by an alternate route having a different transit time than that of the main route, said by-pass line also collecting the growing polymer of a first loop reactor (1) and

sending said growing polymer to an entry point (13) in a second reactor

(2).

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 4 OF 53 USPATFULL on STN

2007:43236 USPATFULL ACCESSION NUMBER:

TITLE: Process for improving the co-polymerization of

ethylene and an olefin co-monomer in

a polymerization loop reactor

INVENTOR(S): Damme, Eric, Arquennes, BELGIUM

NUMBER KIND DATE -----PATENT INFORMATION: US 2007037937 A1 20070215 APPLICATION INFO.: US 2006-499472 A1 20060727 (11)

NUMBER DATE PRIORITY INFORMATION: WO 2005-EP50624 20050214 EP 2004-100568 20040213

Utility DOCUMENT TYPE: FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: FINA TECHNOLOGY INC, PO BOX 674412, HOUSTON, TX,

77267-4412, US

EXEMPLARY CLAIM: 1-3
NUMBER OF DRAWN 1-20

4 Drawing Page(s)

LINE COUNT: 901

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention relates to a process for improving the co-polymerization of ethylene and an olefin co-monomer, preferably hexene, in a polymerization loop reactor characterized in that said process comprises the step of controlling the co-monomer/monomer ratio along the path of the reactor, and in particular by multiple, spat Tally separated, feeding of monomer along the path of the loop reactor. In another aspect, the invention relates to a polymerization loop reactor suitable for the co-polymerization process of

ethylene and an olefin co-monomer, preferably hexene.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 5 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2007:41998 USPATFULL

Method for improving a polymerization reaction by TITLE:

taking out and analysing a sample

INVENTOR(S): Vandaele, Hugo, Sint-Andries, BELGIUM

NUMBER KIND DATE -----US 2007036693 A1 20070215 US 2006-502005 A1 20060809 (11) PATENT INFORMATION: APPLICATION INFO.:

> NUMBER DATE -----

PRIORITY INFORMATION: EP 2004-100599 20040213

PRIORITY INFORMATION.

DOCUMENT TYPE: Utility

APPLICATION

LEGAL REPRESENTATIVE: FINA TECHNOLOGY INC, PO BOX 674412, HOUSTON, TX, 77267-4412, US

NUMBER OF CLAIMS: 17
EXEMPLARY CLAIM: 1-2 1 - 24EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 3 Drawing Page(s) LINE COUNT: 1040

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The invention relates to a device for taking out and analysing a sample from a polymerisation reactor comprising one or more sample conduits (2), for taking a sample out of said reactor and for conducting said sample to one or more sample flash tanks (3), whereby said conduits each are in communication with said reactor (19) and each are provided with at least two sampling valves (4, 5); comprising one or more sample flash tanks (3), for separating said solid particles and evaporated gas, whereby said sample flash tanks are connected to said conduits (2) and provided with means for analysing said evaporated gas (7), and comprising one or more sample receivers (6), for purifying said solid particles, whereby said receivers are connected to said sample flash tanks (3) and provided with means (8) for analysing said solid particles. The invention further relates to a method for improving a polymerisation reaction in a polymerisation reactor.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 6 OF 53 USPATFULL on STN

2006:61382 USPATFULL ACCESSION NUMBER:

Process and apparatus for producing olefin polymers TITLE:

Vuorikari, Marianna, Hamari, FINLAND INVENTOR(S):

Korhonen, Esa, Porvoo, FINLAND Andtsjo, Henrik, Porvoo, FINLAND Zitting, Samuli, Tuusula, FINLAND

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2006052552 US 7115687	A1 B2	20060309 20061003	
APPLICATION INFO.:	US 2003-532607 WO 2003-FI799	A1	20031027 20031027 20050425	(10) PCT 371 date

NUMBER DATE _____

PRIORITY INFORMATION: EP 2002-396161 20021030

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: BIRCH STEWART KOLASCH & BIRCH, PO BOX 747, FALLS

CHURCH, VA, 22040-0747, US

NUMBER OF CLAIMS: 14 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Page(s)

LINE COUNT: 562

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention concerns a process and an apparatus for continuous polymerisation of olefin monomers in a cascade of

polymerisation reactors. According to the process, an olefin

monomer is polymerised first in slurry phase in an

inert hydrocarbon diluent in at least one loop reactor

and then, subsequently, in gas phase in at least one gas phase reactor. According to the invention, a polymer slurry is continuously withdrawn

from the loop reactor and optionally concentrated.

The concentrated slurry is conducted to a high pressure flash unit in order to remove the remaining fluid phase, and fed to the gas phase reactor. With the process described in this invention, it is possible to produce bimodal polyethylene with good properties. The operation of the process is stable because of the truly continuous operation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 7 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2005:313272 USPATFULL TITLE: Double loop technology

INVENTOR(S): Fourage, Louis, Dilbeek, BELGIUM

Damme, Eric, Arquenness, BELGIUM Miserque, Olivier, Mont-Saint-Guibert, BELGIUM

Siraux, Daniel, Naast, BELGIUM

Bodart, Philippe, Clermont sous Huy, BELGIUM

Lewalle, Andre, Bruxelles, BELGIUM Auwera, Marc Van der, Tervuren, BELGIUM Brande, Frans Van den, Mortsel, BELGIUM

Conti, Giacomo, Maurage, BELGIUM
Vandaele, Hugo, Sint-Andries, BELGIUM
Verleysen, Mark, Ekeren, BELGIUM
Camp, Carl Van, Beveren-Waas, BELGIUM
Laurent, Etienne, Seneffe, BELGIUM
Marechal, Philippe, Nivelles, BELGIUM

Moers, Marc, Antwerpen, BELGIUM D'Hooghe, Leopold, Kapellen, BELGIUM Sillis, Marjan, Edegem, BELGIUM Hortman, Kai, Dilbeek, BELGIUM

Folie, Pascal, Courcelles, BELGIUM Oreins, Renaud, Wavre, BELGIUM

PATENT ASSIGNEE(S): ATOFINA Research S.A., Seneffe (Feluy), BELGIUM

(non-U.S. corporation)

NUMBER DATE

PRIORITY INFORMATION: US 2004-544846P 20040213 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: FINA TECHNOLOGY INC, PO BOX 674412, HOUSTON, TX,

77267-4412, US

NUMBER OF CLAIMS: 23 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 51 Drawing Page(s)

LINE COUNT: 9664

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to an apparatus and process for polymerizing olefins. One embodiment comprises polymerizing at

least one monomer in a first loop reactor in the

presence of a catalyst to produce a first polyolefin fraction. A portion

of the first polyolefin fraction is transferred to a second loop

reactor, connected in series with the first loop

reactor. The process further comprises polymerizing in the

second loop reactor at least one monomer in the

presence of a catalyst to produce a second polyolefin fraction in addition to the first polyolefin fraction. The combination of the first and second polyolefin fractions can produce a polymer resin fluff having

bimodal molecular weight distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 8 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2005:299802 USPATFULL TITLE: Cascaded polyolefin slurry

polymerization employing disengagement vessel

between reactors

INVENTOR(S): Mutchler, Joel A., Morris, IL, UNITED STATES

Gupte, Kiran M., Naperville, IL, UNITED STATES
Treptau, Michael H., Channahon, IL, UNITED STATES

PATENT ASSIGNEE(S): Equistar Chemicals L.P., Houston, TX, UNITED STATES

(U.S. corporation)

RELATED APPLN. INFO.: Division of Ser. No. US 2003-396900, filed on 25 Mar

2003, GRANTED, Pat. No. US 6921804

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: BROOKS KUSHMAN P.C., 1000 TOWN CENTER, TWENTY-SECOND

FLOOR, SOUTHFIELD, MI, 48075, US

NUMBER OF CLAIMS: 10 EXEMPLARY CLAIM: 1-18

NUMBER OF DRAWINGS: 2 Drawing Page(s)

LINE COUNT: 618

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A disengagement vessel employing a lock hopper effectively reduces concentration of non-polymer-associated components in the polymer product slurry of a first olefin slurry polymerization reactor, allowing cascading of a second slurry polymerization reactor operating at lesser concentration of comonomers, hydrogen, and other components to produce multicompositional polyolefin polymers and/or polymers having a multimodal monomer distribution, e.g. diblock polymers having substantially non-overlapping

comonomer contents between the blocks.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 9 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:255398 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James A., Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

NUMBER KIND DATE

PATENT INFORMATION:
APPLICATION INFO.:

US 2004198928 A1 20041007 US 2004-827777 A1 20040420 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2003-260010, filed on 11

Mar 2003, PENDING Continuation of Ser. No. US

2001-955729, filed on 19 Sep 2001, PENDING Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, GRANTED,

Pat. No. US 6319997 Division of Ser. No. US

1999-313818, filed on 18 May 1999, GRANTED, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, ABANDONED Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, GRANTED,

Pat. No. US 6281300

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: EXXONMOBIL CHEMICAL COMPANY, P O BOX 2149, BAYTOWN, TX,

77522-2149

NUMBER OF CLAIMS: 27 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Page(s)

LINE COUNT: 1281

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ACCESSION NUMBER: 2004:255397 USPATFULL

Monitoring and control of slurry processes TITLE:

for polymerizing olefins

INVENTOR(S): Battiste, David R., Bartlesville, OK, UNITED STATES

> NUMBER KIND DATE _____

PATENT INFORMATION: APPLICATION INFO.: US 2004198927 A1 20041007 US 2004-825410 A1 20040415 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-705315, filed on 3 Nov

2000, GRANTED, Pat. No. US 6723804

Utility APPLICATION DOCUMENT TYPE: FILE SEGMENT:

LEGAL REPRESENTATIVE: Michael G. Fletcher, Fletcher Yoder, P.O. Box 692289,

Houston, TX, 77269-2289

NUMBER OF CLAIMS: 35 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Page(s) LINE COUNT: 1047

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

Processes, methods and apparatus relating to olefin polymerization include the use of Raman spectrometry to monitor the concentration of reactants, products or other chemical components. One or more polymerizaton conditions are adjusted in response to those monitored concentrations. The present processes, methods and apparatus are applicable with slurry olefin polymerization process, even though such slurry processes contain solid particles were are known to interfere with Raman spectrometry. Furthermore, the present processes, methods and apparatus are applicable where there is some degree of overlap between Raman spectral peaks. Methods of monitoring and controlling olefin polymerization processes, reactants and other components use Raman spectrometry. Apparatus for olefin polymerization reactions have polymerization equipment, at least one Raman probe located in the polymerization equipment, and Raman spectrometry equipment located outside the polymerization equipment and operatively connected to at least one Raman probe.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 11 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:248259 USPATFULL TITLE: Cascaded polyolefin slurry

polymerization employing disengagement vessel

between reactors

Mutchler, Joel A., Morris, IL, UNITED STATES INVENTOR(S):

Gupte, Kiran M., Naperville, IL, UNITED STATES Treptau, Michael H., Channahon, IL, UNITED STATES

Equistar Chemicals L.P., Houston, TX (U.S. corporation) PATENT ASSIGNEE(S):

NUMBER KIND DATE US 2004192861 A1 20040930 US 6921804 B2 20050726 US 2003-396900 A1 20030325 (10) PATENT INFORMATION: APPLICATION INFO.:
DOCUMENT TYPE:
FILE SEGMENT: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: BROOKS KUSHMAN P.C., 1000 TOWN CENTER, TWENTY-SECOND

FLOOR, SOUTHFIELD, MI, 48075

21 NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 2 Drawing Page(s)

LINE COUNT: 689

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A disengagement vessel employing a lock hopper effectively reduces concentration of non-polymer-associated components in the polymer

product slurry of a first olefin slurry polymerization

reactor, allowing cascading of a second slurry

polymerization reactor operating at lesser concentration of

comonomers, hydrogen, and other components to produce multicompositional

polyolefin polymers and/or polymers having a multimodal monomer

distribution, e.g. diblock polymers having substantially non-overlapping

comonomer contents between the blocks.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 12 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:248258 USPATFULL

TITLE: Method and apparatus for high solids slurry

polymerization

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES

Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

NUMBER KIND DATE

PATENT INFORMATION: US 2004192860 A1 20040930 APPLICATION INFO.: US 2004-849393 A1 20040519 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2002-176289, filed on 20

Jun 2002, PENDING Continuation of Ser. No. US

2000-586370, filed on 2 Jun 2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED,

Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Michael G. Fletcher, FLETCHER YODER, P.O. Box 692289,

Houston, TX, 77269-2289

NUMBER OF CLAIMS: 39 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 6 Drawing Page(s)

LINE COUNT: 823

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and

catalyst are circulated in a continuous loop reactor

and product slurry is recovered by means of a continuous product take

off. The continuous product allows operating the reaction at

significantly higher solids content in the

circulating slurry. In a preferred embodiment, the slurry is heated in a flash line heater and passed to a high pressure flash where a majority of the diluent is separated and thereafter condensed by simple heat exchange, without compression, and thereafter recycled. Also an olefin polymerization process operating at higher reactor solids by virtue of more aggressive circulation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 13 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:177718 USPATFULL

TITLE: Proceess and apparatus for separating polymer solids,

hydrocarbon fluids, and purge gas

Verser, Donald W., Houston, TX, UNITED STATES INVENTOR(S):

Burns, David H., Houston, TX, UNITED STATES

Hottovy, John D., Bartlesville, OK, UNITED STATES

NUMBER KIND DATE -----

US 2004136882 A1 20040715 US 2003-700006 A1 20031103 (10) PATENT INFORMATION: APPLICATION INFO.:

Continuation-in-part of Ser. No. US 2003-662249, filed RELATED APPLN. INFO.:

on 15 Sep 2003, PENDING

NUMBER DATE _____

US 2002-411254P 20020916 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Michael G. Fletcher, Fletcher Yoder, P. O. box 692289,

Houston, TX, 77269-2289

NUMBER OF CLAIMS: 43 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 3 Drawing Page(s)

LINE COUNT: 1068

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process and apparatus for separating polymer solids, hydrocarbon fluids, and purge gas in an intermediate pressure zone and a purge zone. The purge gas in the purge zone is used to remove hydrocarbon fluids from the polymer solids, and a stream containing the purge gas and hydrocarbons is passed to a hydrocarbon/purge gas recovery zone. High-purity purge gas from the recovery zone is efficiently used by passing a portion back to the purge zone and another portion to an extruder feed zone. Hydrocarbon fluids separated from polymer solids in the intermediate pressure zone and in the hydrocarbon/purge gas recovery zone are liquefied and passed to a recycle zone, and the hydrocarbons (typically liquid diluent and/or unreacted monomer) are recycled to the reactor without fractionation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 14 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:177717 USPATFULL

Separation of polymer particles and vaporized diluent TITLE:

in a cyclone

Verser, Donald W., Houston, TX, UNITED STATES INVENTOR(S):

Burns, David H., Houston, TX, UNITED STATES

Hottovy, John D., Bartlesville, OK, UNITED STATES

NUMBER KIND DATE PATENT INFORMATION: APPLICATION INFO.:

US 2004136881 A1 20040715 US 2003-699095 A1 20031031 (10) Continuation-in-part of Ser. No. US 2002-176289, filed RELATED APPLN. INFO.:

on 20 Jun 2002, PENDING Continuation of Ser. No. US 2000-586370, filed on 2 Jun 2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED,

Pat. No. US 6239235

Utility DOCUMENT TYPE: FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Michael G. Fletcher, Flectcher Yoder, P. O. Box 692289,

Houston, TX, 77269-2289

NUMBER OF CLAIMS: 27 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 8 Drawing Page(s)

LINE COUNT: 967

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is withdrawn and passed through a heated conduit to a cyclone. The cyclone allows better separation of vaporized diluent. In a preferred embodiment, the slurry is heated in a flashline heater so that a high percentage of the withdrawn diluent is vaporized. The vaporized diluent and concentrated intermediate product are passed to a cyclone where a majority of the vaporized diluent is separated and thereafter condensed by heat exchange, without compression, and recycled to the reactor. Also an apparatus for separating vaporized diluent and polymer particles using a cyclone.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 15 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:159383 USPATFULL

TITLE: Continuous withdrawal from high solids slurry

polymerization

INVENTOR(S): Verser, Donald W., Houston, TX, UNITED STATES

Burns, David H., Houston, TX, UNITED STATES Hein, James E., Houston, TX, UNITED STATES

Rajaendran, George K., Humble, TX, UNITED STATES Hottovy, John D., Barlesville, OK, UNITED STATES

		NUMBER	KIND	DATE	
PATENT INFORMATION:	US	2004122187	A1	20040624	
	US	6815511	B2	20041109	
APPLICATION INFO.:	US	2003-668857	A1	20030923	(10)

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2002-176289, filed on 20 Jun 2002, PENDING Continuation of Ser. No. US 2000-586370, filed on 2 Jun 2000, PENDING Division of

Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED,

Pat. No. US 6239235

NUMBER DATE

PRIORITY INFORMATION: US 2002-413924P 20020925 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Fletcher Yoder, Attn: Michael G. Fletcher, P.O. Box

692289, Houston, TX, 77269-2289

NUMBER OF CLAIMS: 38 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 7 Drawing Page(s)

LINE COUNT: 811

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An improved polymerization process includes withdrawing a portion of a fluid slurry through a plurality of active continuous take off mechanisms, monitoring the pressure of feed material fed to the reactor, and adjusting the continuous take off mechanisms in response to the monitored feed line pressure.

ANSWER 16 OF 53 USPATFULL on STN L7

ACCESSION NUMBER: 2004:97405 USPATFULL

TITLE: Monitoring and control of slurry processes

for polymerizing olefins

Battiste, David R., Bartlesville, OK, United States INVENTOR(S): PATENT ASSIGNEE(S): Chevron Phillips Chemical Company, LP, The Woodlands,

TX, United States (U.S. corporation)

NUMBER KIND DATE -----

US 6723804 B1 20040420 US 2000-705315 20001103

PATENT INFORMATION: US 67238
APPLICATION INFO: US 2000DOCUMENT TYPE: Utility 20001103 (9)

GRANTED FILE SEGMENT: PRIMARY EXAMINER: Teskin, Fred

PRIMARY EXAMINER.

NUMBER OF CLAIMS: 17

EXEMPLARY CLAIM: 1,11

NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)

985

TO DESCRIPTION OF THIS PATENT. Processes, methods and apparatus relating to olefin polymerization include the use of Raman spectrometry to monitor the concentration of reactants, products or other chemical components. One or more polymerizaton conditions are adjusted in response to those monitored concentrations. The present processes, methods and apparatus are applicable with slurry olefin polymerization process, even though such slurry processes contain solid particles were are known to interfere with Raman spectrometry. Furthermore, the present processes, methods and apparatus are applicable where there is some degree of overlap between Raman spectral peaks. Methods of monitoring and controlling olefin polymerization processes, reactants and other components use Raman spectrometry. Apparatus for olefin polymerization reactions have polymerization equipment, at least one Raman probe located in the polymerization equipment, and Raman spectrometry equipment located outside the polymerization equipment and operatively connected to at least one Raman probe.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 17 OF 53 USPATFULL on STN

INVENTOR(S):

ACCESSION NUMBER: 2003:325205 USPATFULL

Slurry Polymerization reactor TITLE:

having large length / diameter ratio, and process of

polymerizing polyolefins in such a reactor Kufeld, Scott E., Houston, TX, UNITED STATES Reid, Thomas A., Deer Park, TX, UNITED STATES Tait, John H., Stafford, TX, UNITED STATES Burns, David H., Houston, TX, UNITED STATES Verser, Donald W., Houston, TX, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Coopersburg, PA, UNITED STATES

Cymbaluk, Teddy H., Seabrook, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES Hottovy, John D., Bartlesville, OK, UNITED STATES

NUMBER KIND DATE ______

US 2003229187 A1 20031211 PATENT INFORMATION:

US 7033545 B2 20060425 US 2002-251662 A1 20020920 (10) APPLICATION INFO.:

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2000-586370, filed

on 2 Jun 2000, PENDING Division of Ser. No. US

1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US

6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: McAndrews, Held & Malloy, Ltd., 34th Floor, 500 West

Madison Street, Chicago, IL, 60661

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 789

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A polymerization loop reactor including a

loop reaction zone, a continuous takeoff, and a fluid slurry disposed in the reaction zone. A generally cylindrical wall defines the loop reaction zone. The length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio greater than 250. The reactor can be charged with a fluid slurry including an olefin monomer reactant, solid olefin polymer particles, and a liquid diluent. The concentration of the solid olefin polymer particles in the slurry can be greater than 40 weight percent based on the weight of polymer particles and the weight of liquid diluent. Also disclosed is a polymerization process carried out by polymerizing, in the loop reaction zone of a reactor as defined above, at least one olefin monomer in a liquid diluent to produce a fluid slurry as defined above.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 18 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:289271 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James A., Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

PATENT ASSIGNEE(S): ExxonMobil Chemical Company, Baytown, TX (U.S.

corporation)

NUMBER KIND DATE US 2003204031 A1 20031030 US 6858682 B2 20050222 PATENT INFORMATION: US 2003-260010 A1 20030311 (10) APPLICATION INFO.:

Continuation of Ser. No. US 2001-955729, filed on 19 RELATED APPLN. INFO.: Sep 2001, PENDING Division of Ser. No. US 2000-679959,

filed on 5 Oct 2000, GRANTED, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, GRANTED, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998,

PENDING Continuation-in-part of Ser. No. US 1998-81392,

filed on 18 May 1998, GRANTED, Pat. No. US 6281300

NUMBER DATE _____

US 1998-78859P 19980320 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: ExxonMobil Chemical Company Law Technology, P. O. Box

2149, Baytown, TX, 77522-2149

NUMBER OF CLAIMS: 27 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Page(s)

LINE COUNT: 1281

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 19 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:283301 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

PATENT ASSIGNEE(S): ExxonMobil Chemical Company, Baytown, TX (U.S.

corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003199645	A1	20031023	
	US 6800698	В2	20041005	
APPLICATION INFO.:	US 2003-260011	A1	20030311	(10)
RELATED APPLN. INFO.:	Continuation of S	Ser. No.	. US 2001-	992770, filed on 6 Nov
	2001, PENDING Con	ntinuat	ion-in-par	t of Ser. No. US
	2001-955729, file	ed on 19	9 Sep 2001	, PENDING Division of
	Ser. No. US 2000-	-679959,	, filed or	5 Oct 2000, GRANTED,
	Pat. No. US 63199	97 Div:	ision of S	Ser. No. US
	1999-313818, file	ed on 18	8 May 1999	, GRANTED, Pat. No. US
	6204344 Continuat	ion-in-	-part of S	Ser. No. US 1998-80412,
	filed on 18 May 1	.998, PE	ENDING Con	tinuation-in-part of
	Ser. No. US 1998-	-81392,	filed on	18 May 1998, GRANTED,
	Pat. No. US 62813	300		

NUMBER	DATE	
1000 700500	100000000	

PRIORITY INFORMATION:
DOCUMENT TYPE:
FILE SEGMENT:

US 1998-78859P Utility APPLICATION

19980320 (60)

LEGAL REPRESENTATIVE: ExxonMobil Chemical Company Law Technology, P. O. Box

2149, Baytown, TX, 77522-2149

NUMBER OF CLAIMS: 54 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 4 Drawing Page(s)

LINE COUNT: 1447

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 20 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:231567 USPATFULL

TITLE: Continuous slurry polymerization

process and apparatus

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003161765	A1	20030828	
	US 7268194	В2	20070911	
APPLICATION INFO.:	US 2002-85809	A1	20020228	(10)
DOCUMENT TYPE:	Utility			

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: EXXONMOBIL CHEMICAL COMPANY, P O BOX 2149, BAYTOWN, TX,

77522-2149

NUMBER OF CLAIMS: 28 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 6 Drawing Page(s)

LINE COUNT: 1802

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (l) as to maintain a desired volume of concentrated

polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 21 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:188649 USPATFULL

Continuous slurry polymerization TITLE:

volatile removal

Kendrick, James A., Baton Rouge, LA, UNITED STATES INVENTOR(S):

Towles, Thomas W., Baton Rouge, LA, UNITED STATES

Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

NUMBER KIND DATE ______ US 2003130442 A1 20030710 US 6670431 B2 20031230 US 2003-375660 A1 20030227 (10) Continuation of Ser. No. US 2001-955729, filed on 19 PATENT INFORMATION:

APPLICATION INFO.:

RELATED APPLN. INFO.:

Sep 2001, PENDING Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, GRANTED, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, GRANTED, Pat. No. US 6204344 Continuation-in-part

of Ser. No. US 1998-80412, filed on 18 May 1998,

PENDING Continuation-in-part of Ser. No. US 1998-81392,

filed on 18 May 1998, GRANTED, Pat. No. US 6281300

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: EXXONMOBIL CHEMICAL COMPANY, P O BOX 2149, BAYTOWN, TX,

77522-2149

NUMBER OF CLAIMS: 27

EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Page(s)

1.INE COUNT: 1272

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to

that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 22 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:137126 USPATFULL

TITLE: Continuous recovery of polymer from a slurry

loop reactor

INVENTOR(S): Salmon, Emigdio J., League City, TX, United States

Equistar Chemicals, LP, Houston, TX, United States PATENT ASSIGNEE(S):

(U.S. corporation)

NUMBER KIND DATE _____ US 6566460 B1 20030520 US 2000-632723 20000804 PATENT INFORMATION: APPLICATION INFO.: 20000804 (9) DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

Wu, David W. PRIMARY EXAMINER: ASSISTANT EXAMINER: Cheung, William K. LEGAL REPRESENTATIVE: Heidrich, William A.

NUMBER OF CLAIMS: 20 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Figure(s); 2 Drawing Page(s)

LINE COUNT: 513

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An apparatus and method for continuously removing polymer from a

pressurized loop olefin polymerization

reactor containing a slurry of polymer particles and

fluids. The slurry is continuously discharged from polymer-rich zones of the reactor and enters one or a series of non-cyclonic flash vessels, in which the particles separate from the fluid. The flash vessel has a conical bottom in which a minimum level of polymer is maintained for a

dynamic seal between the inlet and outlet.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 23 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:134767 USPATFULL

TITLE: High solids slurry polymerization

INVENTOR(S):

Hottovy, John D., Bartlesville, OK, UNITED STATES Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES

Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003092856	A1	20030515	
A DDI TON ETONI THEO	770 0000 001001	3.1	00001100	

APPLICATION INFO.: US 2002-301281 A1 20021120 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility APPLICATION FILE SEGMENT:

LEGAL REPRESENTATIVE: MCANDREWS HELD & MALLOY, LTD, 500 WEST MADISON STREET,

SUITE 3400, CHICAGO, IL, 60661

NUMBER OF CLAIMS: 42 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 642

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. In a preferred embodiment, the slurry is heated in a flash line heater and passed to a high pressure flash where a majority of the diluent is separated and thereafter condensed by simple heat exchange, without compression, and thereafter recycled. Also an olefin polymerization process operating at higher reactor solids

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 24 OF 53 USPATFULL on STN

2003:72122 USPATFULL ACCESSION NUMBER:

TITLE: High solids slurry polymerization

by virtue of more aggressive circulation.

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES

Franklin,, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

NUMBER KIND DATE ______

US 2003050409 A1 20030313 US 2002-228833 A1 20020826 (10) PATENT INFORMATION: APPLICATION INFO.:

Continuation of Ser. No. US 2000-586370, filed on 2 Jun RELATED APPLN. INFO.:

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: MCANDREWS HELD & MALLOY, LTD, 500 WEST MADISON STREET,

SUITE 3400, CHICAGO, IL, 60661

NUMBER OF CLAIMS: 30 EXEMPLARY CLAIM: 1

5 Drawing Page(s) NUMBER OF DRAWINGS:

LINE COUNT: 562

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. In a preferred embodiment, the slurry is heated in a flash line heater and passed to a high pressure flash where a majority of the diluent is separated and thereafter condensed by simple heat exchange, without compression, and thereafter recycled. Also an olefin polymerization process operating at higher reactor solids by virtue of more aggressive circulation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ACCESSION NUMBER: 2003:38297 USPATFULL TITLE: Pumped high solids slurry

polymerization

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES

Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

Phillips Petroleum Company Bartlesville OK UNITED

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK, UNITED

STATES (U.S. corporation)

NUMBER KIND DATE

PATENT INFORMATION: US 2003027944 A1 20030206

APPLICATION INFO:: US 2002-177615 A1 20020620

APPLICATION INFO.: US 2002-177615 A1 20020620 (10) RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Street, Chicago, IL,

60661

NUMBER OF CLAIMS: 8 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 442

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and

catalyst are circulated in a continuous loop reactor

and product slurry is recovered by means of a continuous product take

off. The continuous product allows operating the reaction at

significantly higher solids content in the

circulating slurry. Also an olefin

polymerization process operating at higher reactor solids by

virtue of more aggressive circulation. The fluid slurry is circulated in the loop reaction zone with a pump providing a pressure differential of

at least 18 psi.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 26 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:31060 USPATFULL

TITLE: High solids slurry polymerization

using heat exchange to condense the flashed diluent INVENTOR(S):
Hottovy, John D., Bartlesville, OK, UNITED STATES
Hensley, Harvey D., Bartlesville, OK, UNITED STATES

Przelomski, David J., Houston, TX, UNITED STATES
Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES
Franklin, Robert K., III, Houston, TX, UNITED STATES
Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK, UNITED

STATES (U.S. corporation)

		NUMBER	KIND	DATE	
PATENT INFORMATION:	US	2003023011	A1	20030130	
	US	6806324	В2	20041019	
APPLICATION INFO.:	US	2002-176289	A1	20020620	(10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Floor, Chicago, IL, 60661

NUMBER OF CLAIMS: 3 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 427

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor

and product slurry is recovered by means of a continuous product take off. The product slurry is exposed to a pressure drop in a flash zone, producing a second slurry and vaporized diluent. The vaporized diluent produced in said flash chamber is condensed by heat exchange, without compression.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 27 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:31059 USPATFULL High polymer solids slurry

polymerization

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK, UNITED

STATES (U.S. corporation)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Floor, Chicago, IL, 60661

NUMBER OF CLAIMS: 5
EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 433

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor

and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at

significantly higher solids content in the

circulating slurry. The concentration of solid olefin polymer particles in the slurry in the reaction zone may be maintained at a value of 45 weight percent or higher, based on the weight of polymer particles and the weight of the liquid diluent.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 28 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:31058 USPATFULL TITLE: High polymer solids slurry

polymerization employing 1-olefin comonomer

INVENTOR(S): Franklin, Robert K., III, Houston, TX, UNITED STATES Hottovy, John D., Bartlesville, OK, UNITED STATES Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

Phillips Petroleum Company, Bartlesville, OK (U.S. PATENT ASSIGNEE(S):

corporation)

NUMBER KIND DATE _____ US 2003023009 A1 20030130 US 6743869 B2 20040601 US 2002-176247 A1 20020620 PATENT INFORMATION: APPLICATION INFO.:

Continuation of Ser. No. US 2000-586370, filed on 2 Jun RELATED APPLN. INFO.:

> 2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Floor, Chicago, IL, 60661

NUMBER OF CLAIMS: 9
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 5 Drawing Page(s)
437

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, at least one

olefin comonomer different from the olefin monomer, diluent and catalyst are circulated in a continuous loop

reactor and product slurry is recovered by means of a continuous

product take off. The continuous product allows operating the reaction

at significantly higher solids content in the

circulating slurry.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 29 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:16958 USPATFULL

HIGH SOLIDS, HIGH SPACE-TIME YIELD SLURRY TITLE:

POLYMERIZATION

Hottovy, John D., Bartlesville, OK, UNITED STATES INVENTOR(S):

> Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

Phillips Petroleum Company, Bartlesville, OK, UNITED PATENT ASSIGNEE(S):

STATES (U.S. corporation)

NUMBER KIND DATE _____ PATENT INFORMATION: US 2003012705 A1 20030116 APPLICATION INFO.: US 2002-177624 A1 20020620 A1 20020620 (10) RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Floor, Chicago, IL, 60661

NUMBER OF CLAIMS: 2 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 423

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, at least one

olefin comonomer different from the olefin monomer,

diluent and catalyst are circulated in a continuous loop

reactor and product slurry is recovered by means of a continuous

product take off. The continuous product allows operating the reaction

at significantly higher solids content in the circulating slurry. The polymerization process

operates at a space-time yield of at least 2.18 lb/hr-gal.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 30 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2002:329402 USPATFULL

TITLE: High solids, high ethylene slurry

polymerization

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK (U.S.

corporation)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Chevron Phillips Chemical Company, LP, P.O. Box 4910,

The Woodlands, TX, 77387-4910

NUMBER OF CLAIMS: 4
EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 435

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin polymerization process wherein monomer, diluent and

catalyst are circulated in a continuous loop reactor

and product slurry is recovered by means of a continuous product take

off. The continuous product allows operating the reaction at

significantly higher solids content in the

circulating slurry. The concentration of ethylene in

the circulating slurry is at least 3.67 weight percent and the average

concentration of solid olefin polymer particles is greater $% \left(1\right) =\left(1\right) \left(1\right) \left$

than 40 weight percent.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 31 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2002:308468 USPATFULL

TITLE: Continuous slurry polymerization

process and apparatus

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2002173598	A1	20021121	
	US 6833415	B2	20041221	
APPLICATION INFO.:	US 2002-79226	A1	20020219	(10)
RELATED APPLN. INFO.:	Continuation-in-	-part of	Ser. No.	US 2001-955729, filed
	on 19 Sep 2001,	PENDING	Division	of Ser. No. US
	2000-679959, fil	led on 5	Oct 2000,	, GRANTED, Pat. No. US
	6319997 Division	n of Ser	. No. US 1	1999-313818, filed on
	18 May 1999, GRA	ANTED, Pa	at. No. US	6 6 2 0 4 3 4 4
	Continuation-in-	-part of	Ser. No.	US 1998-80412, filed
	on 18 May 1998,	PENDING	Continuat	tion-in-part of Ser.
	<u>-</u>			ay 1998, GRANTED, Pat.
	No. US 6281300			

NUMBER	DATE			

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: ExxonMobil Chemical Company, P.O. Box 2149, Baytown,

TX, 77522

NUMBER OF CLAIMS: 174 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 1949

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (l) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

L7 ANSWER 32 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2002:243743 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES DePierri, Robert G., Baton Rouge, LA, UNITED STATES

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2001-955729, filed

on 19 Sep 2001, PENDING Division of Ser. No. US

2000-679959, filed on 5 Oct 2000, GRANTED, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on

18 May 1999, GRANTED, Pat. No. US 6204344

Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, PENDING Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, GRANTED, Pat.

No. US 6281300

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: ExxonMobil Chemical Company, P.O. Box 2149, Baytown,

TX, 77522 55

NUMBER OF CLAIMS: 55 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 6 Drawing Page(s)

LINE COUNT: 1442

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 33 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2002:206741 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

NUMBER

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

PATENT INFORMATION: US 2002111441 A1 20020815 APPLICATION INFO.: US 2001-992770 A1 20011106 (9)

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2001-955729, filed

on 19 San 2001 PENDING Division of San No. 118

on 19 Sep 2001, PENDING Division of Ser. No. US

KIND DATE

2000-679959, filed on 5 Oct 2000, PATENTED Division of Ser. No. US 1999-313818, filed on 18 May 1999, PATENTED Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, PENDING Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, PATENTED

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: ExxonMobil Chemical Company, P.O. Box 2149, Baytown,

TX, 77522

NUMBER OF CLAIMS: 54 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 4 Drawing Page(s)

LINE COUNT: 1443

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (l) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 34 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2001:208959 USPATFULL

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James A., Baton Rouge, LA, United States

Towles, Thomas W., Baton Rouge, LA, United States

Roger, Scott T., Zachary, LA, United States

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents Inc., Houston, TX, United

States (U.S. corporation)

NUMBER KIND DATE _____ US 6319997 B1 20011120 US 2000-679959 20001005 PATENT INFORMATION: APPLICATION INFO.: (9)

Division of Ser. No. US 1999-313818, filed on 18 May RELATED APPLN. INFO.: 1999 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998 Continuation-in-part of Ser. No.

US 1998-81392, filed on 18 May 1998

NUMBER DATE

US 1998-78859P 19980320 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Boykin, Terressa M.

LEGAL REPRESENTATIVE: Alexander, D. J., Prodnuk, S. D.

NUMBER OF CLAIMS: 17 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 4 Drawing Figure(s); 3 Drawing Page(s)

1188 LINE COUNT:

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (l) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 35 OF 53 USPATFULL on STN

2001:79259 USPATFULL ACCESSION NUMBER:

High solids slurry polymerization TITLE:

INVENTOR(S): Hottovy, John D., Bartlesville, OK, United States Hensley, Harvey D., Bartlesville, OK, United States Przelomski, David J., Houston, TX, United States Cymbaluk, Teddy H., Pasadena, TX, United States Franklin, III, Robert K., Houston, TX, United States Perez, Ethelwoldo P., Sugar Land, TX, United States

Phillips Petroleum Company, Bartlesville, OK, United PATENT ASSIGNEE(S):

States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6239235	B1	20010529	
APPLICATION INFO.:	US 1997-893200		19970715	(8)
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	Granted			

PRIMARY EXAMINER: Wu, David W. ASSISTANT EXAMINER: Lu, Caixia LEGAL REPRESENTATIVE: Owen, Polly C.

NUMBER OF CLAIMS: 25 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 10 Drawing Figure(s); 5 Drawing Page(s) LINE COUNT: 541

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. In a preferred embodiment, the slurry is heated in a flash line heater and passed to a high pressure flash where a majority of the diluent is separated and thereafter condensed by simple heat exchange, without compression, and thereafter recycled. Also an olefin polymerization process operating at higher reactor solids by virtue of more aggressive circulation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 36 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2001:40558 USPATFULL

Continuous slurry polymerization TITLE:

volatile removal

INVENTOR(S): Kendrick, James A., Baton Rouge, LA, United States

Towles, Thomas W., Baton Rouge, LA, United States

Roger, Scott T., Zachary, LA, United States

PATENT ASSIGNEE(S): Exxon Chemical Patents, Inc., Baytown, TX, United

States (U.S. corporation)

NUMBER KIND DATE -----PATENT INFORMATION: US 6204344 B1 20010320 APPLICATION INFO.: US 1999-313818 19990518 (9) RELATED APPLN. INFO.: Continuation of Ser. No. US 80412

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: Granted

PRIMARY EXAMINER: Boykin, Terressa M.

LEGAL REPRESENTATIVE: Alexander, David J., Prodnuk, Stephen D.

NUMBER OF CLAIMS: 16 EXEMPLARY CLAIM:

4 Drawing Figure(s); 3 Drawing Page(s) NUMBER OF DRAWINGS:

LINE COUNT: 1183

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated

polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 37 OF 53 USPATFULL on STN

ACCESSION NUMBER: 86:21838 USPATFULL

Catalysts, method of preparation and polymerization TITLE:

processes therewith

Miro, Nemesio D., Dewey, OK, United States INVENTOR(S):

Phillips Petroleum Company, Bartlesville, OK, United PATENT ASSIGNEE(S):

States (U.S. corporation)

NUMBER KIND DATE ______ PATENT INFORMATION:
APPLICATION INFO.: US 4582816 19860415 US 1985-704107 19850221 (6) DOCUMENT TYPE: Utility

FILE SEGMENT: Granted PRIMARY EXAMINER: Garvin, Patrick P. LEGAL REPRESENTATIVE: Reiter, Stephen E.

NUMBER OF CLAIMS: 16 EXEMPLARY CLAIM: 1 419 LINE COUNT:

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

Method for the production of milled supports useful for the preparation of mono-1-olefin polymerization catalysts is provided by comminuting Mg(O)mX.sub.2 -m or Mn(O)mX.sub.2 -m, and high density ethylene polymer, optionally in the presence of an aromatic phenol and/or an aluminum halide to produce a composite catalyst support prior to further comminution with a tetravalent titanium halide to produce a first catalyst component and finally admixture of the first catalyst component with an organoaluminum catalyst compound. Polymerization process employing the novel catalyst system thus produced is also provided.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 38 OF 53 USPATFULL on STN

ACCESSION NUMBER: 83:42813 USPATFULL

TITLE: Catalyst, method of producing the catalyst, and

polymerization process employing the catalyst

Capshew, Charles E., Bartlesville, OK, United States INVENTOR(S): Short, James N., Bartlesville, OK, United States Welch, M. Bruce, Bartlesville, OK, United States Dietz, Richard E., Borger, TX, United States

NUMBER KIND DATE

US 4405769 19830920 US 1982-350856 19820222 (6) PATENT INFORMATION:
APPLICATION INFO.:

RELATED APPLN. INFO.: Division of Ser. No. US 1980-177313, filed on 12 Aug

1980, now patented, Pat. No. US 4325837, issued on 20

Apr 1982

DOCUMENT TYPE: Utility

FILE SEGMENT: Granted
PRIMARY EXAMINER: Smith, Edward J.

NUMBER OF CLAIMS: 17 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 8 Drawing Figure(s); 4 Drawing Page(s)

2709 LINE COUNT:

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A transition metal compound and a metal halide compound are chemically combined to form a composition of matter. The composition of matter is rapidly mixed with a precipitating agent to form an active olefin polymerization catalyst.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 39 OF 53 USPATFULL on STN

82:18830 USPATFULL ACCESSION NUMBER:

Catalyst, method of producing the catalyst, and TITLE:

polymerization process employing the catalyst

INVENTOR(S): Capshew, Charles E., Bartlesville, OK, United States

Short, James N., Bartlesville, OK, United States Welch, M. Bruce, Bartlesville, OK, United States Dietz, Richard E., Borger, TX, United States

Phillips Petroleum Company, Bartlesville, OK, United PATENT ASSIGNEE(S):

States (U.S. corporation)

NUMBER KIND DATE -----

US 4325837 19820420 US 1980-177313 19800812 (6) US 4325837

PATENT INFORMATION: US 43258
APPLICATION INFO.: US 1980DOCUMENT TYPE: Utility
Granted FILE SEGMENT: Granted

PRIMARY EXAMINER: Garvin, Patrick
NUMBER OF CLAIMS: 13
EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 8 Drawing Figure(s); 4 Drawing Page(s)

LINE COUNT: 2671

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A transition metal compound and a metal halide compound are chemically combined to form a composition of matter. The composition of matter is rapidly mixed with a precipitating agent to form an active olefin polymerization catalyst under an olefin atmosphere and prepolymer is formed on said catalyst to yield a catalyst capable of producing low fines content polymer.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 40 OF 53 USPATFULL on STN

ACCESSION NUMBER: 76:65153 USPATFULL

TITLE: Prevention of fouling in polymerization reactors Brown, Terry D., Bartlesville, OK, United States INVENTOR(S):

O'Shaughnessy, Marion T., Bartlesville, OK, United

States

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK, United

States (U.S. corporation)

NUMBER KIND DATE US 3995097 19761130 US 1975-613665 19750915 (5) PATENT INFORMATION: APPLICATION INFO.: DOCUMENT TYPE: Utility

FILE SEGMENT: Granted
PRIMARY EXAMINER: Holler, Alan

NUMBER OF CLAIMS: 5 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)

LINE COUNT: 202

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB An olefin is polymerized in a hydrocarbon diluent in a turbulent reaction zone to produce particles of polymer which are substantially insoluble in the diluent. Fouling of the reactor by adherence of polymer particles to the walls of the reactor is reduced by adding to the reaction medium a composition which comprises a mixture of an aluminum or chromium salt of an alkyl salicylic acid and an alkali metal alkyl sulfosuccinate.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 41 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2006:61382 USPAT2

TITLE: Process and apparatus for producing olefin polymers

INVENTOR(S): Vuorikari, Marianna, Hamari, FINLAND

Korhonen, Esa, Porvoo, FINLAND Andtsjo, Henrik, Porvoo, FINLAND Zitting, Samuli, Tuusula, FINLAND

PATENT ASSIGNEE(S): Borealis Technology Oy, Porvoo, FINLAND (non-U.S.

corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 7115687	B2	20061003	
	WO 2004039847		20040513	
APPLICATION INFO.:	US 2003-532607		20031027	(10)
	WO 2003-FI799		20031027	
			20050425	PCT 371 date

NUMBER DATE
----EP 2002-396161 20021030

PRIORITY INFORMATION: EP 2002-39610
DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Teskin, Fred

LEGAL REPRESENTATIVE: Birch, Stewart, Kolasch & Birch, LLP

NUMBER OF CLAIMS: 20 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)

LINE COUNT: 569

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention concerns a process and an apparatus for continuous polymerisation of olefin monomers in a cascade of polymerisation reactors. According to the process, an olefin monomer is polymerised first in slurry phase in an inert hydrocarbon diluent in at least one loop reactor and then, subsequently, in gas phase in at least one gas phase reactor. According to the invention, a polymer slurry is continuously withdrawn from the loop reactor and optionally concentrated.

The concentrated slurry is conducted to a high pressure flash unit in order to remove the remaining fluid phase, and fed to the gas phase reactor. With the process described in this invention, it is possible to produce bimodal polyethylene with good properties. The operation of the process is stable because of the truly continuous operation.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 42 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:248259 USPAT2

Cascaded polyolefin slurry TITLE:

polymerization employing disengagement vessel

between reactors

INVENTOR(S): Mutchler, Joel A., Morris, IL, UNITED STATES

Gupte, Kiran M., Naperville, IL, UNITED STATES

Treptau, Michael H., Channahon, IL, UNITED STATES

Equistar Chemicals L.P., Houston, TX, UNITED STATES PATENT ASSIGNEE(S):

(U.S. corporation)

NUMBER KIND DATE _____ PATENT INFORMATION:

US 6921804 B2 20050726 US 2003-396900 20030325 20030325 (10) APPLICATION INFO.:

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED PRIMARY EXAMINER: Teskin, Fred

LEGAL REPRESENTATIVE: Brooks Kushman P.C.

NUMBER OF CLAIMS: 18 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Figure(s); 2 Drawing Page(s)

LINE COUNT: 650

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A disengagement vessel employing a lock hopper effectively reduces concentration of non-polymer-associated components in the polymer

product slurry of a first olefin slurry polymerization

reactor, allowing cascading of a second slurry

polymerization reactor operating at lesser concentration of

comonomers, hydrogen, and other components to produce multicompositional

polyolefin polymers and/or polymers having a multimodal monomer

distribution, e.g. diblock polymers having substantially non-overlapping

comonomer contents between the blocks.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 43 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:159383 USPAT2

TITLE: Continuous withdrawal from high solids slurry

polymerization

Verser, Donald W., Houston, TX, United States INVENTOR(S):

Burns, David H., Houston, TX, United States Hein, James E., Houston, TX, United States

Rajaendran, George K., Humble, TX, United States Hottovy, John D., Barlesville, OK, United States

Chevron Phillips Chemical Company, LP, The Woodlands, PATENT ASSIGNEE(S):

TX, United States (U.S. corporation)

NUMBER KIND DATE US 6815511 US 2003-668857 PATENT INFORMATION: B2 20041109

APPLICATION INFO.: 20030923 (10)

Continuation-in-part of Ser. No. US 2002-176289, filed RELATED APPLN. INFO.: on 20 Jun 2002 Continuation of Ser. No. US 2000-586370,

filed on 2 Jun 2000 Division of Ser. No. US

1997-893200, filed on 15 Jul 1997, now patented, Pat.

No. US 6239235

NUMBER DATE _____

PRIORITY INFORMATION: US 2002-413924P 20020925 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Lu, Caixia LEGAL REPRESENTATIVE: Fletcher Yoder

NUMBER OF CLAIMS: 13 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 9 Drawing Figure(s); 7 Drawing Page(s) LINE COUNT: 682

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An improved polymerization process includes withdrawing a portion of a fluid slurry through a plurality of active continuous take off mechanisms, monitoring the pressure of feed material fed to the reactor, and adjusting the continuous take off mechanisms in response to the monitored feed line pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 44 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:101933 USPAT2

Process for producing bimodal polyethylene resins TITLE:

Marechal, Philippe, Nivelles, BELGIUM INVENTOR(S):

PATENT ASSIGNEE(S): Total Petrochemicals Research Feluy, Feluy, BELGIUM

(non-U.S. corporation)

NUMBER KIND DATE -----US 7034092 B2 20060425 WO 2002028922 20020411 US 2001-398162 20011002 (10) WO 2001-EP11394 20011002 PATENT INFORMATION: APPLICATION INFO.: 20031117 PCT 371 date

NUMBER DATE

PRIORITY INFORMATION: BE 2000-121646 20001004

DOCUMENT TYPE: Utility GRANTED FILE SEGMENT: FILE SEGMENT: GKANIED PRIMARY EXAMINER: Lu, Caixia

LEGAL REPRESENTATIVE: Jackson, William D.

NUMBER OF CLAIMS: 2.2 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 7 Drawing Figure(s); 6 Drawing Page(s) LINE COUNT: 859

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process for producing bimodal polyethylene resins in two reactors in series, the process comprising producing a first polyethylene resin fraction in a first slurry loop reactor in a diluent in the presence of a catalyst and producing a second polyethylene resin fraction in a second slurry loop reactor, serially connected to the first reactor, in the diluent in the presence of the catalyst, the first polyethylene resin fraction being passed from the first reactor to the second reactor together with the catalyst, one of the first and second reactors producing a resin fraction of higher molecular than the resin fraction produced by the other of the first and second reactors, characterised in that the first reactor is fed with a feed of ethylene and diluent having an ethylene

content of at least 70 wt % based on the weight of the diluent and in that in the first reactor the slurry of polyethylene in the diluent has a solids content of at least 30 wt % based on the weight of the diluent.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 45 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2003:325205 USPAT2

TITLE: Slurry polymerization reactor

having large length/diameter ratio

INVENTOR(S): Kufeld, Scott E., Houston, TX, UNITED STATES

Reid, Thomas A., Deer Park, TX, UNITED STATES Tait, John H., Stafford, TX, UNITED STATES Burns, David H., Houston, TX, UNITED STATES Verser, Donald W., Houston, TX, UNITED STATES

Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Coopersburg, PA, UNITED STATES

Cymbaluk, Teddy H., Seabrook, TX, UNITED STATES
Franklin, Robert K., Houston, TX, UNITED STATES
Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES
Hottovy, John D., Bartlesville, OK, UNITED STATES

PATENT ASSIGNEE(S): Chevon Phillips Chemical Company, LP, The Woodlands,

TX, UNITED STATES (U.S. corporation)

PATENT INFORMATION: US 7033545 B2 20060425 APPLICATION INFO.: US 2002-251662 20020920 (10)

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2000-586370, filed

on 2 Jun 2000, ABANDONED Division of Ser. No. US

1997-893200, filed on 15 Jul 1997, Pat. No. US 6239235

NUMBER DATE

PRIORITY INFORMATION: US 2002-411208P 20020916 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Neckel, Alexa D.

NUMBER OF CLAIMS: 21 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 10 Drawing Figure(s); 5 Drawing Page(s)

LINE COUNT: 839

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymerization loop reactor including a

loop reaction zone, a continuous takeoff, and a fluid slurry disposed in the reaction zone. A generally cylindrical wall defines the loop reaction zone. The length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a

length/diameter ratio greater than 250. The reactor can be charged with

a fluid slurry including an olefin monomer reactant, solid olefin polymer particles, and a liquid diluent. The

concentration of the solid olefin polymer particles in the

slurry can be greater than 40 weight percent based on the weight of polymer particles and the weight of liquid diluent. Also disclosed is a polymerization process carried out by polymerizing, in the loop reaction zone of a reactor as defined above, at least one olefin

monomer in a liquid diluent to produce a fluid slurry as defined above.

ANSWER 46 OF 53 USPAT2 on STN L7

ACCESSION NUMBER: 2003:289271 USPAT2

Continuous slurry polymerization TITLE:

volatile removal

Kendrick, James A., Baton Rouge, LA, United States INVENTOR(S):

> Towles, Thomas W., Baton Rouge, LA, United States Roger, Scott Thomas, Baton Rouge, LA, United States

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents, Inc., Houston, TX, United

States (U.S. corporation)

NUMBER KIND DATE ______

US 6858682 B2 20050222 US 2003-260010 20030311 (10) PATENT INFORMATION: APPLICATION INFO.:

RELATED APPLN. INFO.: Continuation of Ser. No. US 2001-955729, filed on 19 Sep 2001, now abandoned Division of Ser. No. US

2000-679959, filed on 5 Oct 2000, now patented, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, now patented, Pat. No. US 6204344Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, now patented, Pat. No. US 6281300 Continuation-in-part of Ser. No. US 1998-80412, filed

on 18 May 1998, now abandoned

DATE NUMBER _____

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Boykin, Terressa LEGAL REPRESENTATIVE: Reid, Frank E.

NUMBER OF CLAIMS: 25 EXEMPLARY CLAIM: 1

4 Drawing Figure(s); 3 Drawing Page(s) NUMBER OF DRAWINGS:

LINE COUNT: 1340

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 47 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2003:283301 USPAT2

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, United States

Towles, Thomas W., Baton Rouge, LA, United States Roger, Scott Thomas, Baton Rouge, LA, United States

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents, Inc., Houston, TX, United

States (U.S. corporation)

NUMBER KIND DATE

PATENT INFORMATION:
APPLICATION INFO.:
RELATED APPLN. INFO.:

US 6800698 B2 20041005 US 2003-260011 20030311 (10)

Continuation of Ser. No. US 2001-992770, filed on 6 Nov 2001, now abandoned Continuation-in-part of Ser. No. US 2001-955729, filed on 19 Sep 2001, now abandoned Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, now patented, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, now patented, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, now abandoned Continuation-in-part of Ser. No. US

1998-81392, filed on 18 May 1998, now patented, Pat.

No. US 6281300

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Boykin, Terressa

LEGAL REPRESENTATIVE: Reid, Frank E., Griffis, Andrew B.

NUMBER OF CLAIMS: 54 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Figure(s); 4 Drawing Page(s)

LINE COUNT: 1476

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L7 ANSWER 48 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2003:231567 USPAT2

TITLE: Continuous slurry polymerization

process and apparatus

Kendrick, James Austin, Baton Rouge, LA, UNITED STATES INVENTOR(S):

> Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents Inc., Houston, TX, UNITED

STATES (U.S. corporation)

NUMBER KIND DATE ______

US 7268194 B2 20070911 PATENT INFORMATION: APPLICATION INFO.: US 2002-85809 20020228 (10)

Continuation-in-part of Ser. No. US 2002-79226, filed RELATED APPLN. INFO.:

on 19 Feb 2002, Pat. No. US 6833415

Continuation-in-part of Ser. No. US 2001-955729, filed on 19 Sep 2001, ABANDONED Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, ABANDONED Continuation-in-part of Ser. No. US 1998-81392, filed

on 18 May 1998, Pat. No. US 6281300

NUMBER DATE -----

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED PRIMARY EXAMINER: Bhat, N. NUMBER OF CLAIMS: 20 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 8 Drawing Figure(s); 6 Drawing Page(s)

LINE COUNT: 1765

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process of converting a loop reactor into multiple

loop reactors comprising starting with a loop

reactor comprising at least 8 vertical legs, at least two

non-vertical conversion runs, each non-vertical run connected in fluid flow communication with two vertical legs; at least two feed inlets; and at least two continuous discharge conduits; disconnecting at least one connection of each conversion run; and reconnecting each conversion run in fluid flow communication with a different vertical leg in such a

manner to form multiple loop reactors each having at

least one feed inlet and at least one continuous discharge conduit.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 49 OF 53 USPAT2 on STN

2003:188649 USPAT2 ACCESSION NUMBER:

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James A., Baton Rogue, LA, United States

> Towles, Thomas W., Baton Rogue, LA, United States Roger, Scott Thomas, Baton Rogue, LA, United States

ExxonMobil Chemical Patents, Inc., Houston, TX, United PATENT ASSIGNEE(S):

States (U.S. corporation)

NUMBER KIND DATE ______ PATENT INFORMATION: US 6670431 B2 20031230 APPLICATION INFO.: US 2003-375660 20030227

20030227 (10)

RELATED APPLN. INFO.:

Continuation of Ser. No. US 2001-955729, filed on 19 Sep 2001, now abandoned Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, now patented, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, now patented, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998 Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, now patented, Pat.

No. US 6281300

NUMBER DATE

US 1998-78859P 19980320 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Boykin, Terressa M.

NUMBER OF CLAIMS: 19 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 4 Drawing Figure(s); 3 Drawing Page(s)

LINE COUNT: 1262

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of said first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 50 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2003:31060 USPAT2

High solids slurry polymerization TITLE:

using heat exchange to condense the flashed diluent Hottovy, John D., Bartlesville, OK, United States INVENTOR(S): Hensley, Harvey D., Bartlesville, OK, United States Przelomski, David J., Bartlesville, OK, United States Cymbaluk, Teddy H., Bartlesville, OK, United States Franklin, III, Robert K., Bartlesville, OK, United

States

Perez, Ethelwoldo P., Bartlesville, OK, United States Phillips Petroleum Company, Bartlesville, OK, United PATENT ASSIGNEE(S):

States (U.S. corporation)

NUMBER KIND DATE _____ PATENT INFORMATION: US 6806324 B2 20041019 APPLICATION INFO.: US 2002-176289 20020620 (10)

Continuation of Ser. No. US 2000-586370, filed on 20 RELATED APPLN. INFO.:

Jun 2000 Division of Ser. No. US 1997-893200, filed on

15 Jul 1997, now patented, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED PRIMARY EXAMINER: Lu, Caixia

LEGAL REPRESENTATIVE: Conley Rose, P.C., Carroll, Rodney B., Burke, Daniel E.

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 10 Drawing Figure(s); 5 Drawing Page(s)

LINE COUNT: 573

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The product slurry is exposed to a pressure drop in a flash zone,

producing a second slurry and vaporized diluent. The vaporized diluent produced in said flash chamber is condensed by heat exchange, without

compression.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 51 OF 53 USPAT2 on STN

2003:31058 USPAT2 ACCESSION NUMBER:

TITLE: High polymer solids slurry

polymerization employing 1-olefin comonomer

INVENTOR(S): Franklin, III, Robert K., Houston, TX, United States

Hottovy, John D., Bartlesville, OK, United States Hensley, Harvey D., Bartlesville, OK, United States Przelomski, David J., Houston, TX, United States Cymbaluk, Teddy H., Seabrook, TX, United States Perez, Ethelwoldo P., Sugar Land, TX, United States

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK, United

States (U.S. corporation)

NUMBER KIND DATE PATENT INFORMATION: US 6743869 B2 20040601 US 2002-176247 APPLICATION INFO.: 20020620 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun

2000 Division of Ser. No. US 1997-893200, filed on 15

Jul 1997, now patented, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED Lu, Caixia PRIMARY EXAMINER:

Conley Rose, PC, Carroll, Rodney B., Burke, Daniel E. LEGAL REPRESENTATIVE:

NUMBER OF CLAIMS: EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 10 Drawing Figure(s); 5 Drawing Page(s)

LINE COUNT: 461

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

An olefin polymerization process wherein monomer, at least one olefin comonomer different from the olefin monomer, diluent and catalyst are circulated in a continuous loop

reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction

at significantly higher solids content in the

circulating slurry.

ANSWER 52 OF 53 USPAT2 on STN L7

ACCESSION NUMBER: 2002:308468 USPAT2

Continuous slurry polymerization TITLE:

process and appparatus

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, United States

> Towles, Thomas W., Baton Rouge, LA, United States Roger, Scott Thomas, Baton Rouge, LA, United States

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents, Inc., Houston, TX, United

States (U.S. corporation)

NUMBER KIND DATE ______

US 6833415 B2 20041221 US 2002-79226 20020219 (10) PATENT INFORMATION:

APPLICATION INFO.: RELATED APPLN. INFO.:

Continuation-in-part of Ser. No. US 2001-955729, filed on 19 Sep 2001 Division of Ser. No. US 2000-679959, filed on 5 Oct 2000, now patented, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May

1999, now patented, Pat. No. US 6204344

Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, now abandoned Continuation-in-part of Ser. No. US 1998-81392, filed on 18 May 1998, now

patented, Pat. No. US 6281300

DATE NUMBER -----

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Boykin, Terressa M.

LEGAL REPRESENTATIVE: Reid, Frank E.

NUMBER OF CLAIMS: 174 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 7 Drawing Figure(s); 5 Drawing Page(s)

LINE COUNT: 2011

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent comprising diluent, unreacted monomers and polymer solids, comprising a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank with a conical bottom defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the slurry/polymer solids and an exit seal chamber of such diameter (d) and length (1) as to maintain a desired volume of concentrated polymer solids/slurry in the exit seal chamber such as to form a pressure seal while continuously discharging a plug flow of concentrated polymer solids/slurry bottom product of the first flash tank from the exit seal chamber through a seal chamber exit reducer with inclined sides defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ANSWER 53 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2002:243743 USPAT2

TITLE: Continuous slurry polymerization

volatile removal

INVENTOR(S): Kendrick, James Austin, Baton Rouge, LA, UNITED STATES

Towles, Thomas W., Baton Rouge, LA, UNITED STATES Roger, Scott Thomas, Baton Rouge, LA, UNITED STATES DePierri, Robert G., Baton Rouge, LA, UNITED STATES ExxonMobil Chemical Patents Inc., United States (U.S.

PATENT ASSIGNEE(S): ExxonMobil Chemical Patents Inc.,

corporation)

NUMBER KIND DATE

PATENT INFORMATION: US 6926868 B2 20050809 APPLICATION INFO.: US 2001-992590 20011106 (9)

RELATED APPLN. INFO.: Continuation-in-part of Ser. No. US 2001-955729, filed on 19 Sep 2001, ABANDONED Division of Ser. No. US

2000-679959, filed on 5 Oct 2000, Pat. No. US 6319997 Division of Ser. No. US 1999-313818, filed on 18 May 1999, Pat. No. US 6204344 Continuation-in-part of Ser. No. US 1998-80412, filed on 18 May 1998, ABANDONED Continuation-in-part of Ser. No. US 1998-81392, filed

on 18 May 1998, Pat. No. US 6281300

NUMBER DATE

PRIORITY INFORMATION: US 1998-78859P 19980320 (60)

DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Doroshenk, Alexa

LEGAL REPRESENTATIVE: Reid, Frank E., Walsh, Maria C.

NUMBER OF CLAIMS: 42 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 7 Drawing Figure(s); 5 Drawing Page(s)

LINE COUNT: 1407

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process/apparatus is disclosed for continuously separating a liquid

medium comprising diluent and unreacted monomers from a

polymerization effluent of a slurry loop

reactor containing a flow of slurry therein, comprising a discharge conduit extending a distance into the loop

reactor; the conduit having a longitudinal axis and an opening

inside the loop reactor; at least a portion of the

conduit being curved along its longitudinal axis inside the loop reactor; and the opening substantially facing the flow of the

slurry, wherein the discharge conduit is located within a lower leg of the loop reactor such that a continuous discharge of

the polymerization effluent from a slurry reactor

through a discharge valve and transfer conduit into a first intermediate pressure flash tank wherein volatile inert diluent and unreacted monomers are removed and the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash

tank at a lower pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

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L7 ANSWER 15 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2004:159383 USPATFULL

TITLE: Continuous withdrawal from high solids slurry

polymerization

Verser, Donald W., Houston, TX, UNITED STATES INVENTOR(S):

Burns, David H., Houston, TX, UNITED STATES Hein, James E., Houston, TX, UNITED STATES

Rajaendran, George K., Humble, TX, UNITED STATES Hottovy, John D., Barlesville, OK, UNITED STATES

KIND DATE -----US 2004122187 A1 20040624 US 6815511 B2 20041109 US 2003-668857 A1 20030923 (10) PATENT INFORMATION:

APPLICATION INFO.:

Continuation-in-part of Ser. No. US 2002-176289, filed RELATED APPLN. INFO.: on 20 Jun 2002, PENDING Continuation of Ser. No. US

2000-586370, filed on 2 Jun 2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED,

Pat. No. US 6239235

NUMBER DATE _____

US 2002-413924P 20020925 (60) PRIORITY INFORMATION:

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Fletcher Yoder, Attn: Michael G. Fletcher, P.O. Box

692289, Houston, TX, 77269-2289

NUMBER OF CLAIMS: 38 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 7 Drawing Page(s)

LINE COUNT: 811

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

Continuous withdrawal from high solids slurry

polymerization

SUMM [0002] The present invention relates to the slurry

polymerization of olefin monomers. More particularly,

the present invention relates to improved techniques for continuously withdrawing a portion of the fluid slurry from a loop reaction zone and

operating a loop reactor having a plurality of

continuous take off.

SUMM [0003] Polyolefins such as polyethylene and polypropylene may be prepared by particle form polymerization,

also referred to as slurry polymerization. In this technique, feed materials such as diluent, monomer and catalyst are introduced to a loop reaction zone, and a fluid slurry containing solid polyolefin particles in a liquid medium (usually an inert diluent and/or unreacted monomer) is circulated through the loop reaction zone. A portion of the fluid slurry is withdrawn from or taken off the reaction zone so that the solid polyolefin particles can be recovered.

[0004] In continuous loop reactors, the various feed SUMM materials may be introduced to the loop reaction zone in various ways. For example, the monomer and catalyst may be mixed with varying amounts of diluent prior to introduction to the loop reaction zone. The monomer may also be combined with recycled diluent and then fed to the loop reaction zone. In the loop reaction zone, the monomer and catalyst become dispersed in the fluid slurry. As the fluid slurry circulates through the loop reaction zone, the monomer reacts at the catalyst in a polymerization reaction. The polymerization reaction yields solid polyolefin particles in the fluid slurry.

- SUMM [0005] Slurry polymerization in a loop reaction zone has proven commercially successful. The slurry polymerization technique has enjoyed international success with billions of pounds of olefin polymers being so produced annually. With this success has come the desirability, in some situations, of building larger reactors. Larger reactors lead to higher flow rates of fluid slurry. The flow rate inside a loop reactor can be as high as 1,000,000 gallons (3,785,410 liters) per minute or more.
- SUMM [0007] Flow restriction causes loss of flow through the take off valve and may cause more polymer particles to build up. This may cause the reactor pressure to increase, since it is usually controlled (at least partially) by how much the take off valve is opened. If the build up in polymer particles is quicker than the action of the control mechanism for controlling pressure by opening the take off valve, a plugged line and excessive reactor pressures may result. This may be especially severe for fused or atypical polymer chunks that can grow in the loop reactor and have a much larger dimension than the largest polymer particle size. Plugged reactor take off valves can lead to reactor over pressure, downtime, production loss, and in extreme situations, relief of reactor pressure by process safety relief valves.
- [0010] As another aspect, a loop reactor apparatus SUMM is provided. The loop reactor apparatus includes a plurality of major segments and a plurality of minor segments. Each of the major segments is connected at a first end to one of the minor segments, and is connected at a second end to another minor segment. As a result, the major segments and the minor segments form a continuous flow path adapted to convey a fluid slurry. The continuous flow path is substantially free from internal obstructions. The loop reactor also includes a means for introducing an olefin monomer and/or a liquid medium (for example, an inert diluent) into the continuous flow path, a means for introducing a polymerization catalyst into the continuous flow path, and at least two means for continuously taking off a portion of the fluid slurry from the continuous flow path. Alternatively, the loop reactor includes at least four means for continuously taking off a portion of the fluid slurry. Such a loop reactor may have a volume greater than 30,000 gallons, alternatively greater than 35,000 gallons, alternatively greater than 40,000 gallons, alternatively greater than 45,000 gallons, alternatively greater than 50,000 gallons, alternatively greater than 75,000 gallons, alternatively greater than 100,000 gallons.
- SUMM [0011] As yet another aspect, a loop reactor apparatus is provided. The loop reactor apparatus comprises a plurality of major legs and a plurality of minor segments. Each minor segment connects two of the major legs to each other, and by these connections, the legs and the segments comprise a continuous flow path. A monomer feed is attached to one of the legs or segments. At least one catalyst feed is attached to one of the legs or segments. A continuous take off is attached to one of the legs or segments. The continuous take off includes a slurry withdrawal line in fluid communication with the reactor, a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line, and a flush line fluidly connected to provide diluent to the slurry withdrawal line.
- SUMM [0012] In the foregoing loop reactor apparatus, at least two of the minor segments form continual curves. At least two of

the continual curves have one or more continuous take off mechanisms or means attached to them. The loop reactor apparatus may be essentially free of horizontal flow paths in that all the major legs are connected by continual curves.

- SUMM [0013] The apparatus may also include at least one spare continuous take off mechanism or means for continuously withdrawing product slurry. Preferably, the continuous take off mechanism or means comprises a V-ball valve having a nominal body size of at least 11/2 inch. The continuous take off valve may be automatically controlled by a controller, which adjusts the continuous take off valve in response to one or more input signals from pressure transmitters on the monomer feed to the loop reactor (or other means for introducing the olefin monomer to the loop reactor).

 Additionally or alternatively, a pressure transmitter may be disposed on the slurry withdrawal line downstream of the continuous take off valve. The pressure transmitter may be operatively connected to provide a signal to the controller. One or all of the continuous take off mechanisms or means may be automatically controlled in such fashions.
- SUMM [0015] As yet another aspect, a continuous take off mechanism for a loop polymerization reactor is provided. The mechanism comprises a slurry withdrawal line in fluid communication with the reactor, a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line, a flush line fluidly connected to provide diluent to the slurry withdrawal line, and a controller. The controller is configured to receive an input signal from pressure transmitters disposed on a monomer feed and on the slurry withdrawal line downstream of the take off valve. The controller is also configured to send an output signal to adjust the take off valve.
- SUMM [0016] As yet another aspect, a process for starting a loop polymerization reactor is provided. The process comprises feeding ethylene to the reactor and feeding isobutane to the reactor. The mass ratio of ethylene to isobutane fed to the reactor is sufficiently low to avoid plugging of the continuous take off mechanism.
- SUMM [0017] As still another aspect, a process for operating a loop polymerization reactor is provided. The process includes feeding ethylene to the reactor, feeding isobutane to the reactor, feeding a polymerization catalyst to the reactor, circulating a fluid slurry comprising unreacted ethylene and solid polyethylene particles in the isobutane through the reactor, continuously withdrawing a portion of the fluid slurry through a plurality of continuous take off mechanisms, and continuously flushing isobutane through the slurry withdrawal line of an inactive continuous take off mechanism. In this manner, a "hot spare" or "hot standby" is provided for the reactor.
- DRWD [0018] FIGS. 1(a) and (b) show loop reactors and polymer recovery systems.
- DRWD [0022] FIG. 5 is a side view of an elbow of the loop reactor showing a continuous take off mechanism.
- DRWD [0024] FIG. 7 is a side view of an elbow of the loop reactor showing the placement of a plurality of continuous take off mechanisms.
- DRWD [0025] FIG. 8 is a cross section of a portion of a loop reactor and two continuous take off mechanisms.

- DETD [0026] The present process and apparatus relate to continuous take off or withdrawal of a portion of the fluid slurry in a loop reactor. This facilitates operation of the loop reactor at a much higher solids concentration . In particular, the present process and apparatus relate especially to large loop reactors having continuous take off instead of settling legs. The present techniques facilitate reliable operation of such large reactors and reliable withdrawal of product. DETD [0027] The present process and apparatus are applicable to any olefin polymerization in a loop reactor that produces a slurry of solid polyolefin particles in a liquid medium. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The present process and apparatus are particularly suitable for the homo polymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.1 to 4 10 weight percent, preferably 0.01 to 5 weight percent, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient
- polyethylene herein.

 [0031] Additional details regarding loop reactor apparatus and polymerization processes may be found in U.S. Pat. Nos. 4,674,290; 5,183,866; 5,565,174; 5,624,877; 6,005,061; 6,045,661; 6,051,631; 6,114,501; and 6,420,497, which are also incorporated by reference herein.

comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer. Such polymers are still referred to as

- DETD [0032] Referring now to the drawings, FIG. 1(a) shows a loop reactor 10 having eight vertical segments 12, upper horizontal segments 14 and lower horizontal segments 16. The horizontal segments may be replaced by curved segments or continual curves so that the reactor contains essentially no horizontal flow paths, as shown in FIG. 1(b). In FIG. 1(a), these upper and lower horizontal segments define upper and lower zones of horizontal flow. In FIG. 1(b), the upper and lower curved segments 14a and 16a take the places of the horizontal segments. The reactor is cooled by means of heat exchangers formed by pipe 12 and jacket 18. Each segment is connected to the next segment by a smooth bend or elbow 20 thus providing a continuous flow path substantially free from internal obstructions. The fluid slurry is circulated by means of an impeller driven by motor 24. Monomer (and comonomer, if any) and fresh diluent are introduced through lines 26 and 28 respectively which can enter the reactor directly at one (as shown in FIG. 1(a)) or a plurality (as shown in FIG. 1(b)) of locations or can combine with recycled diluent line 30 as shown. In FIG. 1(b) the recycle diluent line splits to provide four feed points 30a, 30b, 30c, and 30d. During initial start-up of a loop reactor having one or more continuous take off mechanisms, it has been found desirable to increase the amount of recycled diluent fed to the reactor, with respect to the ethylene fed to the reactor. For example, a 1:1 mass flow ratio of ethylene and recycled isobutane during initial start-up has been found to reduce plugging of the continuous take off mechanism. Smaller mass flow ratios, for example, 4:5 or 2:3, may also be used. Catalyst is introduced via catalyst introduction means 32 which provides a zone (location) for catalyst introduction.
- DETD [0033] A continuous take off mechanism for withdrawing an intermediate product slurry is designated broadly by reference character 34.

 Continuous take off mechanism 34 is located in or adjacent to an end, preferably a downstream end, of one of the lower horizontal segments 16

or the lower curved segments 16a or adjacent or on a connecting elbow 20. One advantage of the continuous take off mechanism 34 is that it can eliminate the need for horizontal segments. Settling legs typically were attached to horizontal segments. Using continuous take off mechanisms facilitates the use of preferable curved segments. The continuous take off mechanism 34 is shown at the downstream end of a lower horizontal segment of the loop reactor. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. It is presently preferred to locate a continuous take off at an upward flowing elbow (an elbow in which the fluid slurry turns upward to flow up a vertical segment). However, the continuous take off mechanism can be attached to any segment, elbow or curve.

DETD [0034] As described in U.S. Pat. No. 6,239,235, polymerization processes utilizing continuous take off instead of a traditional settling leg for slurry take off are favored for larger reactors. U.S. Pat. No. 6,239,235 (which is incorporated herein by reference) discloses an olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and slurry is withdrawn by use of a continuous take off mechanism. The process may be employed in loop reaction zones of greater than 30,000 gallons. Also, reactor polymer solids concentrations of greater than 40 weight percent, and preferably greater than 50 weight percent are discussed.

DETD [0038] Vaporized diluent exits the high pressure flash chamber 38 through conduit 42 for further processing which includes condensation by simple heat exchange using recycle condenser 50, and return to the loop reactor, without the necessity for compression, via recycle diluent line 30. Recycle condenser 50 can utilize any suitable heat exchange fluid known in the art under any conditions known in the art. However preferably a fluid at a temperature that can be economically provided is used. A desirable temperature range for this fluid is 40 degrees F. to 130 degrees F. Polymer particles are withdrawn from high pressure flash chamber 38 via line 44 for further processing using techniques known in the art. The polymer particles may be passed to low pressure flash chamber 46 (or directly to a purge zone) and thereafter recovered as polymer product via line 48. Separated diluent passes through compressor 47 to line 42. This high pressure flash design is broadly disclosed in U.S. Pat. No. 4,424,341, which is hereby incorporated by reference.

DETD [0040] FIG. 2 shows a curved segment 16a with continuous take off mechanism 34 in more detail. The continuous take off mechanism typically at least includes a slurry withdrawal line in fluid communication with the reactor and a valve for controlling the flow of slurry through that line. The continuous take off mechanism shown in FIG. 2 comprises a take off cylinder 52 attached to the reactor with a flange 53, a slurry withdrawal line 54, an emergency shut off valve 55 (or block valve), a proportional motor valve 58 (the CTO valve) to regulate flow and a flush line 60. The cylinder 52 need not extend into the reactor; indeed, extending a protrusion into a loop slurry reactor may result in polymer build-up around the protrusion. However, in some circumstances the cylinder may extend into the reactor. Diluent input is generally held constant, the proportional motor valve 58 being used to control the rate of continuous withdrawal to maintain the total reactor pressure within designated set points. A manual flash line may also be connected with the flash line downstream of the proportioned motor valve 58. Diluent input may be adjusted based upon logic which calculates and controls the weight percent of solids in the reactor.

DETD [0043] It has been found desirable to maintain at least one continuous

DETD

DETD

take off mechanism in inactive status by closing block valve 66 (or another downstream valve) rather than ram valve 62. A continuous take off is inactive if it is not being used to withdraw product slurry as part of the normal commercial production of the polyolefin. The flush line 70 and flush valve 72 may also be operated to automatically feed diluent to slurry withdrawal line 54 if a downstream valve or block valve is shut or plugged. By closing block valve 66 or other downstream valve but leaving ram valve 62 open, the continuous take off mechanism can be maintained as a "hot spare" or "hot standby" that may rapidly, essentially instantaneously, remotely, and/or automatically be put into use if needed. By maintaining a "hot spare" continuous take off mechanism, an additional continuous take off mechanism can rapidly (within 1 minute or less) be put into operation during certain situations and prevent high pressure in the reactor. The continuous take off mechanism can be maintained as a hot spare by continually flushing diluent through flush line 70 and flush valve 72 when the block valve 66 is closed. Alternatively, a hot spare may have the block valve open and another downstream valve (for example, the proportional motor valve 58 or the CTO valve 74) closed. In that case, the flush line 70 and flush valve 72 may be locate downstream of block valve 66. The flush line 70 and flush valve 72 may also be operated to automatically feed diluent to slurry withdrawal line 54 if the continuous take off mechanism is shut or plugged. It is highly desirable to equip the loop reactor with at least one continuous take off mechanism to exist as a spare, in case the active continuous take off mechanism become plugged, which is a significant risk during operation. [0045] In FIG. 4, an automatic control is shown in the form of a programmable controller 76, which adjusts the CTO valve 74 in response to one or more input signals. The input signals in FIG. 4 are from pressure transmitters 78 and 79 on feed lines 80 and 81 to the loop reactor. However, the input signal may be indicative of the pressure (or other parameter) in the reactor or in downstream equipment, such as the flash line or a flash chamber. [0048] The continuous take off cylinders are smaller than the conventional settling legs. Yet three 2-inch ID continuous take off appendages can remove as much product slurry as 14 eight-inch ID settling legs. This is significant because with commercial loop reactors of 15,000-18,000 gallon capacity, 6 eight-inch settling legs are required. It is not desirable to increase the size of the settling legs because of the difficulty of making reliable valves for larger diameters. Reactors of 30,000 gallons or more benefit from the present process and apparatus. Generally the continuous take off cylinders will have a nominal internal diameter within the range of from about 1 inch to about 8 inches. Preferably they will be from about 2 to about 3 inches internal diameter. As the line extends from the reactor, the diameter may gradually increase or decrease to provide the desired effect on pressure and/or flow within the line. The line may gradually reduce in diameter leading to the CTO valve (and gradually increase in diameter after passing the CTO valve) in order to adapt to the size of the control valve, maintain a high slurry velocity and/or not provide sharp edges that can lead to polymer buildup. For example, a 2 inch line diameter may gradually taper to 1.5 inch diameter over 3 inches before the CTO valve 74, and then reverse-taper from 1.5 inch diameter to 2 inch over a similar distance after the CTO valve 74. In FIG. 4, tapered conduits or swedges 86 and 88 are shown before and after the CTO valve 74. Nonetheless, it is important to ensure there are no sudden enlargements or contractions of the lines' diameters, as that could lead to plugging. Preferably, the housing of the CTO valve is flanged for attachment to hollow appendages through which the withdrawn slurry flows. For the same reason, it is important to ensure smooth connections

between pipes and no misalignments between pipe connections.

[0051] FIG. 7 is a side view of an elbow of the loop reactor showing the placement of a plurality of continuous take off mechanisms. Four continuous take off mechanisms are shown, though only two are active; the other two continuous take off mechanisms are provided as options or spares. In FIG. 7, the continuous take off 34d and 34e are located at curve angles 30 degrees and 60 degrees on the downward flow leg (that is, the leg through which the fluid slurry is flowing downward), and the continuous take off 34f and 34g at 70 degrees and 40 degrees on the upward flow leg (that is, the leg through which the fluid slurry is flowing upward). In general, ranges of 0-60 degrees on a downward flow leg and a range of 30-90 degrees, more preferably 70-90 degrees, on an upward flow leg are preferred.

[0052] FIG. 8 shows a cross section of a horizontal segment of a DETD loop reactor and two continuous take off mechanisms 34b and 34c. These continuous take off mechanisms 34b and 34c are disposed along a horizontal segment of the loop reactor 10 and form angle gamma with the bottom edge of the horizontal segment. The angle gamma is greater than 0 degrees and less than or equal to 90 degrees. This arrangement is especially suitable for a horizontal loop reactor which does not have upward or downward flowing elbows. In other words, this arrangement is suitable for the horizontal loop reactor where the major segments and minor segments are all disposed in an essentially horizontal plane. The horizontal segments need not extend along a perfectly horizontal axis but rather may be substantially horizontal. For example, a horizontal segment may be positioned at a tilt or angle that is between 0 and 15 degrees from a true horizontal plane.

DETD [0054] It has been discovered that automatic and/or regular movement of the continuous take off valve is useful for reducing or avoiding instances of plugging in the valve. Regular movement of the continuous take off valve may attain a reduction in instances of continuous take off valve plugging. The short localized pressure pulse created by the movement of the continuous take off valve can reduce plugging by forcing accumulated polymer chunks or particles through the valve. However, the duration and magnitude of the pressure pulse is not so large as to significantly affect the average pressure of the loop reactor. By moving the continuous take off valve at regular intervals, regardless of the detection of plugging, the operator can clear the continuous take off valve, ensure regular production of polymer and avoid plugging problems before they occur. CLM What is claimed is:

6. A process for operating a loop polymerization reactor, the process comprising: feeding at least one olefin monomer and diluent to the reactor; feeding a polymerization catalyst to the reactor; circulating a fluid slurry comprising unreacted ethylene and solid polyethylene particles in the diluent through the reactor; continuously withdrawing a portion of the fluid slurry through a plurality of active continuous take off; and continuously flushing diluent through an inactive continuous take

CLM What is claimed is:
10. A process for starting a loop polymerization
reactor, the process comprising: feeding ethylene to
the reactor; and feeding isobutane to the reactor; wherein the mass
ratio of ethylene to isobutane fed to the reactor is
sufficiently low to avoid plugging of a continuous take off.

CLM What is claimed is:

off.

- 14. A loop reactor apparatus comprising: a plurality of major segments; a plurality of minor segments, each minor segment connecting two of the major segments to each other, whereby the segments comprise a continuous flow path; at least one monomer feed fluidly attached to the continuous flow path; at least one catalyst feed fluidly attached to the continuous flow path; and at least two active continuous take offs each attached to the continuous flow path, and each of the continuous take offs comprises: a slurry withdrawal line in open communication with the reactor; and a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line; at least one inactive continuous take off attached to the continuous flow path, the continuous take off comprising: a slurry withdrawal line in open communication with the reactor; and a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line.
- CLM What is claimed is:
 15. A loop reactor apparatus according to claim 14
 wherein the inactive continuous take off further comprises a flush line fluidly connected to provide diluent to the slurry withdrawal line.
- CLM What is claimed is:

 16. A loop reactor apparatus according to claim 14

 wherein the take off valves V-ball valves having a nominal body size of at least 11/2 inch.
- CLM What is claimed is:
 17. A loop reactor apparatus according to claim 16
 wherein the continuous take offs further comprise a block valve disposed along the slurry withdrawal line upstream of the V-ball valve and downstream of the continuous flow path.
- CLM What is claimed is:
 18. A loop reactor apparatus according to claim 14
 further comprising; a monomer pressure transmitter disposed on the
 monomer feed; and a controller that is configured to receive an input
 signal from the monomer pressure transmitter, and the controller is
 configured to send an output signal to adjust at least one of the
 continuous take offs.
- CLM What is claimed is:

 19. A loop reactor apparatus according to claim 18,
 further comprising: a pressure transmitter disposed on the slurry
 withdrawal line downstream of the take off valve and operatively
 connected to provide a signal to the controller; and wherein the take
 off valve is automatically controlled by the controller, which adjusts
 the take off valve in response to one or more input signals from the
 pressure transmitters on the monomer feed and the slurry withdrawal
 line.
- CLM What is claimed is:
 20. A loop reactor apparatus according to claim 14
 wherein the slurry withdrawal line narrows before the take off valve and widens after the slurry withdrawal line.
- CLM What is claimed is:
 21. A loop reactor apparatus according to claim 14
 wherein the continuous flow path has a volume of greater than 30,000 gallons.

- CLM What is claimed is:
 22. A loop reactor apparatus according to claim 14
 wherein the continuous flow path has a volume of greater than 35,000
 gallons.
- CLM What is claimed is:
 23. A loop reactor apparatus according to claim 14
 wherein at least two active continuous take offs and at least one
 inactive continuous take offs are disposed on one of the minor segments.
- CLM What is claimed is: 24. A loop reactor apparatus according to claim 14 comprising at least four of the continuous take offs.
- CLM What is claimed is:
 25. A loop reactor apparatus according to claim 14
 wherein the continuous flow path is essentially free of horizontal flow paths.
- CLM What is claimed is:
 26. A loop reactor apparatus according to claim 14
 wherein the minor segments are continual curves defining a portion of a circle, and the circle has a radius of at least 3 feet.
- CLM What is claimed is:
 27. A loop reactor apparatus according to claim 14
 wherein the major segments are substantially horizontal.
- CLM What is claimed is:
 28. A loop reactor apparatus according to claim 27
 wherein the minor segments are substantially horizontal.
- CLMWhat is claimed is: 29. A loop reactor apparatus comprising: a pipe loop reactor adapted for conducting an olefin polymerization process comprising polymerizing at least one olefin monomer in a liquid diluent to produce a fluid slurry comprising solid olefin polymer particles in the liquid diluent, the pipe loop reactor having a volume of greater than 30,000 gallons; a plurality of elongated hollow appendages in direct fluid communication with the pipe loop reactor adapted for continuous removal of a portion of the fluid slurry from the pipe loop reactor; a feed for introducing an olefin monomer and diluent into the pipe loop reactor; a feed for introducing a polymerization catalyst into the pipe loop reactor; and a circulator for circulating the fluid slurry through the pipe loop reactor.
- CLM What is claimed is:
 30. A loop reactor apparatus according to claim 29,
 further comprising: a pressure transmitter in fluid communication with
 at least one of the elongated hollow appendages; and a controller that
 is configured to receive an input signal from the pressure transmitter
 and the controller is configured to send an output signal to adjust the
 flow of fluid slurry through the elongated hollow appendage.
- CLM What is claimed is: 31. A loop reactor apparatus according to claim 29,

further comprising: a pressure transmitter in fluid communication with the olefin monomer feed; and a controller that is configured to receive an input signal from the pressure transmitter and the controller is configured to send an output signal to adjust the flow of fluid slurry through the elongated hollow appendage.

- CLM What is claimed is:
 - 32. A loop reactor apparatus according to claim 29 comprising from four to twelve elongated hollow appendages.
- CLM What is claimed is:
 - 33. A loop reactor apparatus according to claim 29 wherein the pipe loop reactor is essentially horizontal, and the elongated hollow appendages are attached to substantially horizontal segments of the pipe loop reactor.
- CLM What is claimed is:

 34. A loop reactor apparatus according to claim 29,
 further comprising at least one inactive elongated hollow appendage
 having a flush line connected, and the flush line is adapted to
 continuously flush diluent through the inactive elongated hollow
 appendage.
- CLM What is claimed is:
 35. A loop reactor apparatus according to claim 29,
 further comprising a controller for opening an inactive elongated hollow
 appendage when an active elongated hollow appendage is plugged.
- CLM What is claimed is:

 36. A continuous take off mechanism for a loop polymerization reactor, the mechanism comprising: (1) a slurry withdrawal line in fluid communication with the reactor; (2) a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line; (3) a flush line fluidly connected to provide diluent to the slurry withdrawal line; and (4) a controller configured to receive an input signal from at least one pressure transmitter disposed on a monomer feed, and the controller is configured to send an output signal to adjust the take off valve.

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L7 ANSWER 16 OF 53 USPATFULL on STN

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TITLE: Monitoring and control of slurry processes

for polymerizing olefins

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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Monitoring and control of slurry processes for

polymerizing olefins

AΒ Processes, methods and apparatus relating to olefin polymerization include the use of Raman spectrometry to monitor the concentration of reactants, products or other chemical components. One or more polymerizaton conditions are adjusted in response to those monitored concentrations. The present processes, methods and apparatus are applicable with slurry olefin polymerization process, even though such slurry processes contain solid particles were are known to interfere with Raman spectrometry. Furthermore, the present processes, methods and apparatus are applicable where there is some degree of overlap between Raman spectral peaks. Methods of monitoring and controlling olefin polymerization processes, reactants and other components use Raman spectrometry. Apparatus for olefin polymerization reactions have polymerization equipment, at least one Raman probe located in the polymerization equipment, and Raman spectrometry equipment located outside the polymerization equipment and operatively connected to at least one Raman probe.

SUMM One type of polymerization process employs a slurry as the reaction mixture. In slurry polymerization processes, solid olefin polymers such as polypropylene, polyethylene and copolymers, are formed under polymerization conditions that include a slurry as the reaction mixture. The slurry comprises the solid olefin polymer particles suspended in a liquid diluent that is inert in the polymerization reaction and in which the polymer is insoluble under polymerization conditions. Typically, slurry polymerization processes are conducted in a relatively high-pressure continuous reactor, such as a loop reactor. Such reactors may be operated at pressures of about 600 psi, for example, and at temperatures of about 60 degrees C. to about 100 degrees C. In many situations, slurry polymerization processes are relatively more commercially desirable than other polymerization processes.

SUMM In the slurry polymerization process, components such as one or more monomers, a diluent, and a catalyst system and possibly other reactants (such as, for example, comonomers or hydrogen) are introduced to the polymerization reactor to form a reaction mixture. The reaction mixture is maintained under polymerization conditions for formation of polyolefin. After a suitable period, the slurry or a portion thereof is discharged from the reactor through a product take-off line into a settling leg. The solid polyolefin settles out from the slurry, leaving a clear liquid comprising diluent and reactants such as the monomer. The clear liquid and solid polyolefin then may then re-mix as they are transferred to one or more separation chambers or flash tanks where, for example, they are flashed to a low pressure such as about 15 or 20 psi. Some slurry loop polymerization equipment includes both a high pressure flash tank and a low pressure flash tank. Further information and details of slurry polymerization processes and loop reactors, including examples of suitable reaction conditions as well as control schemes for other important variables, such as solids concentration and production rate, can be found in U.S. Pat. No. 3,998,995 and U.S. Pat. No. 3,257,363, which are incorporated herein by reference.

- Current methods of monitoring slurry polymerization processes and the components (reactants, products, and diluent) in such processes are less than optimal for several reasons. In loop polymerization processes, monomer and co-monomer content have typically been determined by gas chromatography ("GC") analysis of the flash gas, that is, the gas released at one of the flash tanks where pressure is released. For example, U.S. Pat. No. 3,257,363 discloses methods of controlling the composition of the reaction mixture in a loop polymerization reactor wherein a gas chromatographic analyzer may be used to determine the amounts of ethylene and 1-butene reactants from a polymer-free off-gas line or with a sample stream from anywhere in the reaction system.
- Analyses of slurry olefin polymerization processes in situ, that is, within a slurry loop polymerization reactor or associated equipment, have been difficult if not impossible to do, since such olefin polymerization reactions are carried out at high pressures. However, spectrophotometric apparatus such as a spectrograph and a radiation source can be situated in a location remote from the polymerization reactor that is to be analyzed in situ, the sampling site being connected to the apparatus by radiation conduits comprising fiber optic cables.
- SUMM There are several factors that have favored the use of gas chromatography as an analytical method over Raman spectrometry with olefin polymerization processes. In general, it is recognized by those familiar with Raman spectrometry that the presence of solid particles in a solution to be analyzed will significantly reduce the Raman shift observed. In particular, slurry olefin polymerization processes include solid polyolefin particles in the slurry. Also, the reactants and products in olefin polymerization processes may have peaks in their respective Raman spectra that are relatively close together, such as when ethylene is employed as a monomer and hexene is employed as a co-monomer. For example, ethylene and hexene produce similar peaks in their Raman spectra. Ethylene exhibits a peak at 1620 cm.sup.-1 while hexene exhibits a peak at 1640 cm.sup.-1. As a result, it may be difficult to distinguish between ethylene and hexene, and there is likely to be some overlap in certain peaks. Thus, it would appear necessary to employ high resolution Raman spectrometry equipment to analyze the components of certain olefin polymerization processes. Furthermore, Raman spectrometry equipment, particularly high resolution Raman spectrometry equipment, is relatively expensive, which would generally discourage its use with industrial processes. Gas chromatography equipment has historically been less costly than high resolution Raman spectrometry equipment. Furthermore, gas chromatography sampling systems are well established. Also, gas chromatography equipment tends to provide information that is more readily usable, whereas Raman spectrometry equipment tends to produce information that requires additional analysis. Engineers and operators tend to prefer equipment that provides a relatively simple reading rather than a spectrum.
- SUMM A process for olefin polymerization in a slurry comprising solid polyolefin and a diluent is provided. The process comprises the steps of contacting in a reaction mixture under slurry polymerization conditions: (i) at least one reactant including at least one olefin monomer and optionally at least one comonomer and optionally hydrogen and (ii) a heterogeneous catalyst system comprising one or more catalytic metal compounds and one or more

co-catalysts; (b) making a polyolefin; and (c) monitoring the process by using Raman spectrometry equipment to provide an output signal representative of one or more of reactants or the polyolefin; and (c). The output signal is generally representative of a concentration of either one of the reactants or the products, though the signal that comes directly from the Raman probe will be converted to a concentration value as described herein to provide the output signal.

- SUMM The monitoring may be done using Raman spectrometry equipment to analyze effluent, such as the effluent from a loop polymerization reactor.
- As yet another aspect, an apparatus for olefin polymerization is provided. The apparatus comprises polymerization equipment comprising a polymerization reactor for slurry polymerization of one or more olefins, wherein the slurry comprises solid polymer particles and a diluent; at least one inlet to the reactor for providing chemical components of the polymerization; at least one outlet from the reactor for removing product from the polymerization reactor; at least one Raman probe located in the polymerization equipment, where the Raman probe provides an output signal; Raman spectrometry equipment located outside the polymerization equipment and operatively connected to at least one Raman probe.
- DRWD FIG. 1 is a diagram of a loop polymerization reactor comprising Raman spectrometry equipment for monitoring a slurry olefin polymerization process.
- DETD Some embodiments described herein are described in the terms of the polymerization of ethylene. However, the present processes and apparatus may be employed with any process where it is desired to monitor and control polymerization of an olefin. It is particularly applicable to the operation of loop reactors which produce polyethylene or polypropylene under slurry polymerization conditions.

 Polymerization conditions generally include the concentration of reactants, products and other chemical components, temperature, pressure, withdrawal rate from the reactor, and circulation rate within the reactor
- Preferably, a Raman fiber optic probe is employed in the present processes, methods and apparatus. Suitable probes include the InPhotonics RP-785-01-05-SMA probe and the InPhotonics RP-785-100-01SMA probe. The InPhotonics probe is preferred for analysis where there are solids present such as in the slurry olefin polymerization reactor. It has been found that other Raman fiber optic probes are not presently operable in a slurry olefin polymerization reactor. Another supplier of Raman fiber optic probes is Kaiser Optical Systems, Inc., which is similar to the InPhotonics probe in good performance in rejecting back scattering radiation. In general, a suitable Raman fiber optic probe may be constructed by soldering metal coated, fused silica fiber optic cables into a protective metal sheath. This probe design provides a simple, reliable method of optically sampling and remotely monitoring a chemical composition in a harsh physical environment of a manufacturing process. It may be advisable to position optical filters near the sample to remove background-inducing radiation caused by the fused silica core of the fiber optic cable.
- DETD Referring to FIG. 1, there is illustrated a loop polymerization reactor 11 and associated equipment for the polymerization process. This loop polymerization reactor provides a continuous path of circulation of the

reaction slurry or reaction mixture. In this embodiment, the loop reactor 11 is jacketed by heat exchange sections 12 which are connected by line 13 and contain a heat exchange medium supplied by line 14 and removed by line 16 for maintaining the loop reactor 11 at a desirable temperature. The reactor 11 is provided with suitable agitation or circulating equipment, such as a propeller or stirrer 18 driven by a motor 17. In this type of reactor, the reaction mixture is circulated through the reactor at a velocity that provides highly turbulent flow, for example, about 21 feet/second. The reaction effluent from the reactor 11 is withdrawn through a product take-off line 19 and passed to a settling leg 24 which can be a drain or vertical leg. In preferred embodiments, the reaction effluent is a slurry made up of polyethylene, unreacted ethylene , unreacted comonomer, and isobutane, and the catalyst is generally contained in the polyethylene. A suitable apparatus for controlling the removal of polymerization reaction effluent is disclosed in U.S. Pat. No. 5,565,174, which is incorporated herein by reference. The withdrawal of effluent is regulated by suitable equipment, such as a flow rate control valve 21, pressure regulator controller 22, and pressure sensor and transmitter 23, such withdrawal equipment being dependent upon reactor pressure.

DETD A catalyst system, such as chromium oxide on silica or a silica-titanium catalyst, is provided from conduit 58 and introduced to reactor 11 after mixing with some diluent from line 59 in catalyst tank 57. Any catalyst system suitable for polymerizing olefin may be employed with the present processes and apparatus. In slurry polymerization processes, it is particularly preferred to employ heterogeneous catalyst systems comprising one or more catalytic metal compounds, and co-catalysts such as an alkylaluminum or aluminoxane, perhaps with a support material such as silica. In FIG. 1, the catalyst flow rate is regulated by flow control apparatus such as a suitable rotary valve 61 driven by a motor 62, which is controlled by speed rate controller 63. The concentration of catalyst in the reaction mixture can vary widely, particularly depending on the type of catalyst used, however, it will generally comprise 0.001 to 5 percent by weight based on the liquid hydrocarbon diluent. The catalyst injection rate can be controlled by means of a heat balance computer or other means to maintain a constant rate of polymer production.

The polymerization reaction, or one or more its components or conditions, may be monitored. The monitoring equipment shown in FIG. 1 includes a Raman probe 66, which for clarity is shown as a box surrounding the loop reactor 11 but which is typically disposed mostly or entirely within the reactor 11. The Raman probe 66 provides an output signal which is representative of the Raman spectrum of the chemical components in reactor 11 or some portion of those components. The output signal from Raman probe 66 is provided to an analyzer 68 which in turn provides a signal to computer 67. Information transmittal paths and signal paths are shown in FIG. 1 by dashed lines. The physical form of those paths may vary. In computer 67, the Raman spectrum is monitored, and the polymerization process may be controlled manually or automatically in response to the spectrum. For example, computer 67 may send a signal (represented in FIG. 1 by dashed lines) to one or more of controllers 60, 65, 75 to adjust the amounts of reactants or diluent added to the loop reactor or the amount of material withdrawn. Alternatively, computer 67 may send a signal to one or more of motor 17 (to adjust the circulation of reaction mixture), pressure regulator controller 22 (to control the withdrawal of product), or valve 61 (to control the amount of catalyst provided to reactor 11).

DETD In an example of the development of a calibration model, a Raman Systems

R-2001C spectrometer was placed in a polyethylene pilot plant control room, and an InPhotonics RP-785-100-01-SMA probe was placed about 100 feet away in the settling leg product take-off line of a polyethylene reactor. A process gas chromatograph measured the concentrations of ethylene, hexene and isobutane in the reactor flash gas. The spectra from the Raman Systems R-2001C unit and the GC analyzer data were entered into the Grams/32 PLS-1 model to build the calibration model.

- DETD By use of this model, we were able to predict ethylene and hexene concentrations within 11% of the GC analyzer value, which is an acceptable error range. With this level of accuracy, it is possible to effectively monitor the concentration of ethylene and hexene in the liquid phase of the reactor.
- DETD In the present methods and apparatus, there are two aspects with respect to the placement of the Raman probe. In one aspect, the Raman probe is placed in the reactor such that it analyzes the slurry having a concentration of solid polymer in a liquid containing diluent and reactants. The slurry may typically comprise 50 weight percent solids. The Raman probe is exposed to and measures polymer, diluent and reactants. It has been observed that the polyolefin particles tend to diffract or scatter the emitted light such that it is not observed by the Raman probe. As a result, the presence of polyolefin particles may lower the signal intensity to about one-tenth of what it would be in a clear liquid. One problem with Raman spectrometry in a slurry is that a substantial amount of scattered light does not come back to the detector. One response to this problem has been to place the Raman probe in the product removal area of the slurry loop polymerization process.
- DETD It has been found that monitoring in the settling leg using Raman spectrometry is better and quicker than monitoring at the flash tanks using gas chromatography. The flash chamber is downstream from the settling leg, and in the dual-stage flash system frequently used with loop reactors operating at pressures of about 600 psi, the reaction mixture is dropped from about 600 psi to about 300 psi in the first flash chamber and then down to 15 psi in the second flash chamber. The gas chromatograph in the first flash chamber takes about six minutes for its analysis and the gas chromatograph in the low pressure flash chamber takes about six minutes for its analysis. One must add those two times together, and so it takes 12 to about 15 minutes to complete the entire gas chromatographic analysis of the flash gas. Further, it is disadvantageous to employ two numbers which are obtained at two different pressures (for example, 300 psi and 15 psi) and it may lead to some errors in the gas chromatographic method. In contrast, Raman analysis of the clear liquid in the product take-off line is a few seconds away from the reactor, and an analysis may be obtained more quickly.
- DETD Furthermore, it may be advantageous to develop a calibration model for Raman spectrometry equipment to be used in a slurry olefin polymerization process by calibrating in a 1-hexene process. For example, the Raman probe may be placed in the sampling line for the gas chromatograph system of a 1-hexene process. Then, data from the Raman system and the gas chromatograph system are obtained for the same liquid. Those data may be used to correlate the Raman spectra to concentrations determined by the gas chromatograph and develop a calibration model.
- DETD However, in a slurry polymerization process, the Raman probe may also be placed in the reactor where it is in contact with the slurry. It has been observed that there may be about a ten-fold reduction in signal, but some of the newer probes, such as from InPhotonics, are capable of detecting the lower levels of scattered

light from the slurry.

CLM What is claimed is:

1. A process for olefin polymerization in a slurry comprising solid polyolefin and a diluent, said process comprising the steps of: (a) contacting in a reaction mixture under slurry polymerization conditions: (i) at least one reactant comprising at least one olefin monomer and optionally at least one comonomer and optionally hydrogen; (ii) a heterogeneous catalyst system comprising one or more catalytic metal compounds and one or more co-catalysts; (b) making a polyolefin; and (c) monitoring the process by using Raman spectrometry equipment to provide an output signal representative of one or more of said reactants or said polyolefin; and (d) adjusting the olefin polymerization process in response to the output signal provided by the Raman spectrometry equipment by adjusting one or more polymerization conditions selected from the group consisting of polymerization temperature, polymerization pressure, withdrawal of said reaction mixture from said reactor, and circulation rate of said mixture within said reactor.

CLM What is claimed is:

10. A process for olefin polymerization in a slurry comprising solid polyolefin and a diluent, said process comprising the steps of: (a) contacting in a reaction mixture under slurry polymerization conditions within a loop polymerization reactor: (i) at least one reactant comprising at least one olefin monomer and optionally at least one comonomer and optionally hydrogen; (ii) a heterogeneous catalyst system comprising one or more catalytic metal compounds and one or more cocatalysts; (b) making a polyolefin; and (c) monitoring the process by using Raman spectrometry equipment by analyzing effluent from said loop polymerization reactor to provide an output signal representative of one or more of said reactants or said polyolefin.

CLM What is claimed is:

11. A process for olefin polymerization in a slurry comprising solid polyolefin and a diluent, the process comprising the steps of: (a) contacting in a reaction mixture under slurry polymerization conditions: (i) at least one reactant comprising at least one olefin monomer and optionally at least one comonomer and optionally hydrogen; (ii) a heterogeneous catalyst system comprising one or more catalytic metal compounds and one or more cocatalysts; (b) making a polyolefin; (c) monitoring the process by using Raman spectrometry equipment to provide an output signal representative of one or more of said reactants or the polyolefin; and (d) adjusting the olefin polymerization process in response to the output signal provided by the Raman spectrometry equipment; wherein the olefin polymerization process is performed in two or more reactors connected in series, wherein effluent from an upstream reactor is provided as input to a downstream reactor, wherein the monitoring step comprises determining a concentration of the monomer in the effluent by Raman spectrometry equipment, and the adjusting step comprises providing an amount of monomer or comonomer in addition to the effluent to the downstream reactor.

TITLE: Continuous recovery of polymer from a slurry

loop reactor

INVENTOR(S): Salmon, Emigdio J., League City, TX, United States PATENT ASSIGNEE(S): Equistar Chemicals, LP, Houston, TX, United States

(U.S. corporation)

NUMBER KIND DATE

PATENT INFORMATION: US 6566460 B1 20030520 APPLICATION INFO.: US 2000-632723 20000804 (9)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Wu, David W.

ASSISTANT EXAMINER: Cheung, William K. LEGAL REPRESENTATIVE: Heidrich, William A.

NUMBER OF CLAIMS: 20 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Figure(s); 2 Drawing Page(s)

LINE COUNT: 513

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Continuous recovery of polymer from a slurry loop reactor

AB An apparatus and method for continuously removing polymer from a pressurized loop olefin polymerization reactor containing a slurry of polymer particles and fluids. The slurry is continuously discharged from polymer-rich zones of the reactor and enters one or a series of non-cyclonic flash vessels, in which the particles separate from the fluid. The flash vessel has a conical bottom in which a minimum level of polymer is maintained for a dynamic seal between the inlet and outlet.

SUMM U.S. Pat. No. 3,242,150 to Scoggin teaches a conventional means for removing solid polymer from a vertical loop slurry reactor. Solid polymer accumulates in a small-diameter tube or settling leg extending from the lower side of the loop reactor. The polymer then exits through a valve which periodically opens fully and closes. Scoggin also discloses a two-valve arrangement by which a bottom valve is closed and an upper valve opens to trap polymer product therein, then the upper valve is closed and the bottom valve opens to allow the polymer to escape toward the product recovery zone.

In one aspect the invention relates to a method of continuously removing polymer from a pressurized loop polymerization reactor containing a slurry of polymer particles and liquids, and an apparatus suitable for this method. A slurry of polymer particles is continuously conveyed from polymer-rich zones of the reactor through a discharge means and a transfer line. The slurry enters a non-cyclonic flash vessel maintained at a lower pressure, whereupon the particles separate and settle to the bottom of the flash vessel. In one embodiment, more than one flash vessel is employed. The flash vessel has vertical sidewalls and a conical bottom in which a minimum level of polymer is maintained for a dynamic seal.

DRWD FIG. 1 briefly shows an embodiment which describes a loop reactor containing polyethylene in a hydrocarbon diluent kept in constant circulation by pump with desired amount of polymer which is continuously withdrawn via a discharge port through a line to a flash vessel.

DRWD FIG. 2 shows a cross-sectional view of the reactor loop and one embodiment of an apparatus.

- DETD The present invention relates to an improved apparatus and method for separating and removing liquid from the solid polymer product in a slurry exiting an olefin polymerization reactor. Those skilled in the art will recognize, however, that the invention applies to different polymerization systems involving monomers, comonomers, diluents, reactor types and process conditions other than those specifically exemplified below.
- DETD The invention is especially applicable to slurry loop polymerization systems, typically an endless loop of pipe. One example is a vertical loop reactor such as that used in the Phillips high density polyethylene process. A second example is a horizontal loop reactor such as the so-called "Petro" reactors developed and originally licensed by National Petro Chemicals.
- DETD Slurry loop reactors operate at high temperatures and elevated pressures typically greater than 400 psia, often greater than 600 psi. Particular conditions are chosen based on the diluent and the reactants.
- DETD Continuous, rather than batch, withdrawal of polymer can be advantageously applied to many types of polymerization reactors, including vertical and horizontal slurry loop reactors
- DETD In horizontal loop reactors such as Petro reactors the location of the polymer withdrawal system in the loop has not heretofore been seen as critical. Polymer slurry containing, for example, about 30 weight percent solids could be withdrawn from any convenient point along the reactor loop then sent to a hydrocyclone to be separated into a solids-rich portion (about 40% solids) and a solids-lean portion (about 20% solids). The solids-rich portion would be conveyed to a flash vessel while the solids-lean portion would be returned to the reactor. However, the ability of a hydrocyclone to process a higher weight percent solids stream without blockages was seen as a limitation to substantially increasing the solids concentration in the effluent stream from the reactor. This also had the effect of limiting operation at higher solids concentration in the reactor.
- DETD We have noted that the slurry circulating within a horizontal loop reactor is not uniform. A significant differential in the concentration of polymer solids exists or can be created between certain locations, and efficiencies can be achieved by particular placement of the polymer discharge means.
- DETD Although a horizontal loop reactor is oriented substantially in the horizontal plane it is typically tilted by less than ten degrees, preferably less than five degrees; more preferably about one to two degrees. This tilt provides a high point where gases can accumulate and be withdrawn during the reactor filling step. We have discovered additional benefits by locating the polymer discharge means at or near the lowest point of the reactor.
- DETD With reference to FIG. 1, a loop reactor 101 contains polyethylene in a hydrocarbon diluent kept in constant circulation by pump 103. Fresh feed, typically monomer, co-monomer, catalyst and additional diluent, enter the reactor via multiple lines which are represented here by line 107. A desired amount of the polymer is continuously withdrawn via discharge port 108 through line 109 to flash vessel 121. The amount withdrawn is dependent upon the reactor conditions and the polymer production rate. In a preferred control scheme, the fresh monomer is added to the reactor at a constant rate, and flow through the discharge means is controlled by a valve 112 in response to reactor pressure. Thus the rate of polymer discharge may vary, but it is continuous rather than intermittent or cycling.

- DETD In a preferred embodiment, a stream of polymer slurry at a concentration of 30-50 % or more solids is continuously discharged from the loop reactor into a high pressure flash vessel where it is flashed from an operating pressure between 635 to 675 psia, preferably about 655 psia (about 640 psig) to near 20-25 psia (about 5-10 psig). The physical location of the reactor discharge nozzle is at the bottom of the pipe (6 o'clock position) and upstream of the suction of the reactor circulating pump.
- DETD FIG. 2 shows a cross-sectional view of the reactor loop 101 and one embodiment of an apparatus at port 108 to allow continuous withdrawal of a predetermined amount of polymer slurry from the reactor. During start-up of the reactor and normal operation of the reactor, valve 112 permits flow of slurry through line 116. Valve 112 is adjustable and automatically controls reactor set pressure. For example, as fresh feed is added to the reactor, valve 112 opens to increase the discharge and thus maintain constant pressure.
- DETD Continuous withdrawal has certain advantages. Plugging is minimized as the flow of polymer does not stagnate even though polymerization may continue in this line. Continuous withdrawal also allows the reactor to be maintained at a steady state pressure without the fluctuations seen with cycling discharge systems, which can cause the reactor pressure to vary by at least 10 and often 20 psig or more. Product quality can improve from more stable process conditions and a more constant concentration of reactants, as the ethylene flowrate to the reactor remains nearly constant.
- DETD This example illustrates one aspect of the invention incorporating a specific reactor discharge nozzle on a horizontal loop "Petro" reactor used for ethylene polymerization in an isobutane diluent.
- CLM What is claimed is:

 1. A method of continuously obtaining polymer product from an olefin polymerization reactor comprising an endless loop of pipe, the method comprising: circulating within the loop a slurry of polymer particles and liquids while maintaining the reactor at a first pressure above 400 psia; continuously conveying an amount of the polymer particles from the reactor first through a discharge means located below a horizontal midline of a cross-section of the reactor pipe and then through a transfer line; and receiving the polymer particles at the inlet of a non-cyclonic primary flash vessel having vertical sidewalls and a conical bottom and maintained at a second pressure less than 25 psia, whereupon the particles settle to the bottom of the flash vessel.
- CLM What is claimed is:
 2. The method of claim 1 in which the reactor is a horizontal loop reactor.
- CLM What is claimed is:
 8. The method of claim 7 in which the reactor is a horizontal loop reactor.
- CLM What is claimed is:
 9. The method of claim 7 in which the reactor is a vertical loop reactor.
- CLM What is claimed is:
 12. The method of claim 1 in which the reactor is a vertical loop reactor.
- CLM What is claimed is:

18. A method of continuously obtaining polymer product from an olefin polymerization reactor comprising an endless loop of pipe, the method comprising: circulating within the loop a slurry of polymer particles and liquids while maintaining the reactor at a first pressure above 400 psia; continuously conveying an amount of the polymer particles from the reactor first through a discharge means located below a horizontal midline of a cross-section of the reactor pipe and then through a transfer line; receiving the polymer particles at the inlet of a non-cyclonic primary flash vessel having vertical sidewalls and a conical bottom and maintained at a second pressure less than 25 psia, whereupon the particles settle to the bottom of the flash vessel; and including the additional step, before the polymer particles enter the primary flash vessel, of receiving the polymer particles at the inlet of an intermediate non-cyclonic flash vessel with an upper section having vertical sidewalls and the inlet being tangential to the sidewall, a conical bottom with an outlet therein, and operated at a third pressure intermediate between the first and second pressures.

CLMWhat is claimed is:

> 20. A method of continuously obtaining polymer product from an olefin polymerization reactor comprising an endless loop of pipe, the method comprising: circulating within the loop a slurry of polymer particles and liquids while maintaining the reactor at a first pressure above 400 psia; continuously conveying an amount of the polymer particles from the reactor first through a discharge means located below a horizontal midline of a cross-section of the reactor pipe and then through a transfer line; receiving the polymer particles at the inlet of a non-cyclonic primary flash vessel having vertical sidewalls and a conical bottom and maintained at a second pressure less than 25 psia, whereupon the particles settle to the bottom of the flash vessel; removing a portion of the polymer particles via an outlet at the bottom of the flash vessel while retaining an amount of particles sufficient to maintain a dynamic seal between the inlet and the outlet of the vessel and maintaining a level which fills the conical bottom of the vessel.

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PATENT ASSIGNEE(S):

ANSWER 25 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2003:38297 USPATFULL Pumped high solids slurry TITLE:

polymerization

Hottovy, John D., Bartlesville, OK, UNITED STATES INVENTOR(S): Hensley, Harvey D., Bartlesville, OK, UNITED STATES Przelomski, David J., Houston, TX, UNITED STATES

Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES Franklin, Robert K., III, Houston, TX, UNITED STATES Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES Phillips Petroleum Company, Bartlesville, OK, UNITED

STATES (U.S. corporation)

KIND DATE NUMBER

US 2003027944 A1 20030206 US 2002-177615 A1 20020620 PATENT INFORMATION: APPLICATION INFO.: 20020620 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun 2000, PENDING Division of Ser. No. US 1997-893200, filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Herbert D. Hart III, McAndrews, Held & Malloy, Ltd.,

500 West Madison Street, 34th Street, Chicago, IL,

60661

NUMBER OF CLAIMS: 8 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 442

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Pumped high solids slurry polymerization

AB An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. Also an olefin polymerization process operating at higher reactor solids by virtue of more aggressive circulation. The fluid slurry is circulated in the loop reaction zone with a pump providing a pressure differential of

the loop reaction zone with a pump providing a pressure differential of at least 18 psi.

SUMM [0002] Addition polymerizations are frequently carried out in a liquid which is a solvent for the resulting polymer. When high density (linear) ethylene polymers first became commercially available in the 1950's this was the method used. It was soon discovered that a more efficient way to produce such polymers was to carry out the

polymerization under slurry conditions. More specifically, the polymerization technique of choice became continuous

slurry polymerization in a pipe loop reactor with the product being taken off by means of settling legs which operated on a batch principle to recover product. This technique has enjoyed international success with billions of pounds of ethylene polymers being so produced annually. With this success has come the desirability of building a smaller number of large reactors as opposed to a larger number of small reactors for a given plant capacity.

SUMM [0003] Settling legs, however, do present two problems. First, they represent the imposition of a "batch" technique onto a basic continuous process. Each time a settling leg reaches the stage where it "dumps" or "fires" accumulated polymer slurry it causes an interference with the flow of slurry in the loop reactor upstream and the recovery system downstream. Also the valve mechanism essential to periodically seal off the settling legs from the reactor upstream and the recovery system downstream requires frequent maintenance due to the difficulty in maintaining a tight seal with the large diameter valves needed for sealing the legs.

SUMM [0005] In spite of these limitations, settling legs have continued to be employed where olefin polymers are formed as a slurry in a liquid diluent. This is because, unlike bulk slurry polymerizations (i.e. where the monomer is the diluent) where solids concentrations of better than 60 percent are routinely obtained, olefin polymer slurries in a diluent are generally limited to no more than 37 to 40 weight percent solids. Hence settling legs have been believed to be necessary to give a final slurry product at the exit to the settling legs of greater than 37-40 percent. This is because, as the name implies, settling occurs in the legs to thus increase the solids concentration of the slurry finally recovered as product slurry.

- SUMM [0008] It is a further object of this invention to operate a slurry olefin polymerization process in a diluent at a reactor solids concentration high enough to make direct continuous product takeoff commercially viable;
- SUMM [0009] It is a further object of this invention to operate a slurry olefin polymerization process in a diluent at higher circulation velocities.
- SUMM [0010] It is yet a further object of this invention to operate a slurry olefin polymerization process in a diluent in a reaction zone of greater than 30,000 gallons; and
- SUMM [0011] It is still yet a further object of this invention to provide a loop reactor apparatus having a capacity of greater than 30,000 gallons and having a continuous take off means.
- SUMM [0013] In accordance with another aspect of this invention, a loop reactor olefin polymerization process is carried out by operating at a higher circulation velocity for a given reactor pipe diameter.
- DRWD [0016] FIG. 1 is a schematic perspective view of a loop reactor and polymer recovery system;
- DRWD [0020] FIG. 5 is a side view of an elbow of the loop reactor showing both a settling let and continuous take off assemblies;
- [0026] Surprisingly, it has been found that continuous take off of DETD product slurry in an olefin polymerization reaction carried out in a loop reactor in the presence of an inert diluent allows operation of the reactor at a much higher solids concentration. Commercial production of predominantly ethylene polymers in isobutane diluent has generally been limited to a maximum solids concentration in the reactor of 37-40 weight percent. However, the continuous take off has been found to allow significant increases in solids concentration. Furthermore, the continuous take off itself brings about some additional increase in solids content as compared with the content in the reactor from which it takes off product because of the placement of the continuous take off appendage which selectively removes a slurry from a stratum where the solids are more concentrated. Hence concentrations of greater than 40 weight percent are possible in accordance with this invention.
- DETD [0030] The present invention is applicable to any olefin polymerization in a loop reactor utilizing a diluent so as to produce a product slurry of polymer and diluent. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The invention is particularly suitable for the homopolymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.01 to 10, preferably 0.01 to 5, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer.
- DETD [0033] Referring now to the drawings, there is shown in FIG. 1 a loop reactor 10 having vertical segments 12, upper

horizontal segments 14 and lower horizontal segments 16. These upper and lower horizontal segments define upper and lower zones of horizontal flow. The reactor is cooled my means of two pipe heat exchangers formed by pipe 12 and jacket 18. Each segment is connected to the next segment by a smooth bend or elbow 20 thus providing a continuous flow path substantially free from internal obstructions. The polymerization mixture is circulated by means of impeller 22 (shown in FIG. 8) driven by motor 24. Monomer, comonomer, if any, and make up diluent are introduced via lines 26 and 28 respectively which can enter the reactor directly at one or a plurality of locations or can combine with condensed diluent recycle line 30 as shown. Catalyst is introduced via catalyst introduction means 32 which provides a zone (location) for catalyst introduction. The elongated hollow appendage for continuously taking off an intermediate product slurry is designated broadly by reference character 34. Continuous take off mechanism 34 is located in or adjacent to a downstream end of one of the lower horizontal reactor loop sections 16 and adjacent or on a connecting elbow 20.

- DETD [0034] The continuous take off appendage is shown at the downstream end of a lower horizontal segment of the loop reactor which is the preferred location. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. However, the continuous take off appendage can be located on any segment or any elbow.
- DETD [0041] As can be seen from the relative sizes, the continuous take off cylinders are much smaller than the conventional settling legs. Yet three 2-inch ID continuous take off appendages can remove as much product slurry as 14 8-inch ID settling legs. This is significant because with current large commercial loop reactors of 15,000-18000 gallon capacity, six eight inch settling legs are required. It is not desirable to increase the size of the settling legs because of the difficulty of making reliable valves for larger diameters. As noted previously, doubling the diameter of the pipe increases the volume four-fold and there simply in not enough room for four times as many settling legs to be easily positioned. Hence the invention makes feasible the operation of larger, more efficient reactors. Reactors of 30,000 gallons or greater are made possible by this invention. Generally the continuous take off cylinders will have a nominal internal diameter within the range of 1 inch to less than 8 inches. Preferably they will be about 2-3 inches internal diameter. [0048] Commercial pumps for utilities such as circulating the reactants DETD
- in a closed loop reactor are routinely tested by their manufacturers and the necessary pressures to avoid cavitation are easily and routinely determined.
- DETD [0049] A four vertical leg polymerization reactor using a 26 inch Lawrence Pumps Inc. pump impeller D51795/81-281 in a M51879/FAB casing was used to polymerize ethylene and hexene-1. This pump was compared with a 24 inch pump which gave less aggressive circulation (0.66 ft of pressure drop vs 0.98). This was then compared with the same more aggressive circulation and a continuous take off assembly of the type shown by reference character 34 of FIG. 5. The results are shown below.

DATA TABLE

26 in Pump +

Description 24 in Pump 26 in Pump CTO

Date of Operation Oct. 4-9, 1994 May 24-28, 1995 Nov. 15-18, 1996

Avg. Reactor Solids	39	45	53
Concentration,			
wt % Polymer Produc-	40.1	40.7	39.9
tion Rate, mlbs/h		10.7	33.3
Reactor Circula-	430	691	753
tion Pump Power,			
kw			
Circulation Pump	14.3	22.4	23.7
Pressure Diff, ps			
Circulation Pump	61.8	92.5	92.4
Head, ft			
Reactor Slurry	39	46	45
Flow			
Rate, mGPM	0 524	0.550	0 500
Reactor Slurry	0.534	0.558	0.592
Density, gm/cc Reactor Tempera-	215.6	218.3	217.0
ture, F.	213.0	210.5	217.0
Ethylene	4.43	3.67	4.9
Concentration,	1.15	3.0,	1.5
wt %			
Hexene-1	0.22	0.17	0.14
Concentration,			
wt %			
Reactor Heat	270	262	241
Transfer Coeffi-			
cient			
Reactor Inside	22.0625	22.0625	22.0625
Diameter, inches			
Reactor Volume,	18700	18700	18700
gal	. 041	0.41	0.41
Reactor Length, f		941	941
Pressure Drop per	0.000	0.098	0.098
Foot of Reactor, ft/ft			
10/10			

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L7 ANSWER 30 OF 53 USPATFULL on STN

ACCESSION NUMBER: 2002:329402 USPATFULL

TITLE: High solids, high ethylene slurry

polymerization

INVENTOR(S): Hottovy, John D., Bartlesville, OK, UNITED STATES Hensley, Harvey D., Bartlesville, OK, UNITED STATES

Przelomski, David J., Houston, TX, UNITED STATES
Cymbaluk, Teddy H., Pasadena, TX, UNITED STATES
Franklin, Robert K., III, Houston, TX, UNITED STATES
Perez, Ethelwoldo P., Sugar Land, TX, UNITED STATES

PATENT ASSIGNEE(S): Phillips Petroleum Company, Bartlesville, OK (U.S.

corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2002187081	A1	20021212	
APPLICATION INFO.:	US 2002-176201	A1	20020620	(10)
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RELATED APPLN. INFO.: Continuation of Ser. No. US 2000-586370, filed on 2 Jun 2000, PENDING Division of Ser. No. US 1997-893200,

filed on 15 Jul 1997, GRANTED, Pat. No. US 6239235

DOCUMENT TYPE: Utility FILE SEGMENT: APPLICATION

LEGAL REPRESENTATIVE: Chevron Phillips Chemical Company, LP, P.O. Box 4910,

The Woodlands, TX, 77387-4910

NUMBER OF CLAIMS: 4
EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 5 Drawing Page(s)

LINE COUNT: 435

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI High solids, high ethylene slurry polymerization

AB An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. The concentration of ethylene in the circulating slurry is at least 3.67 weight percent and the average concentration of solid olefin polymer particles is greater than 40 weight percent.

SUMM [0002] Addition polymerizations are frequently carried out in a liquid which is a solvent for the resulting polymer. When high density (linear) ethylene polymers first became commercially available in the 1950's this was the method used. It was soon discovered that a more efficient way to produce such polymers was to carry out the polymerization under slurry conditions. More specifically, the polymerization technique of choice became continuous slurry polymerization in a pipe loop reactor with the product being taken off by means of settling legs which operated on a batch principle to recover product. This technique has enjoyed international success with billions of pounds of ethylene polymers being so produced annually. With this success has come the desirability of building a smaller number of large reactors as opposed to a larger number of small reactors for a given plant capacity.

SUMM [0003] Settling legs, however, do present two problems. First, they represent the imposition of a "batch" technique onto a basic continuous process. Each time a settling leg reaches the stage where it "dumps" or "fires" accumulated polymer slurry it causes an interference with the flow of slurry in the loop reactor upstream and the recovery system downstream. Also the valve mechanism essential to periodically seal off the settling legs from the reactor upstream and the recovery system downstream requires frequent maintenance due to the difficulty in maintaining a tight seal with the large diameter valves needed for sealing the legs.

SUMM [0005] In spite of these limitations, settling legs have continued to be employed where olefin polymers are formed as a slurry in a liquid diluent. This is because, unlike bulk slurry polymerizations (i.e. where the monomer is the diluent) where solids concentrations of better than 60 percent are routinely obtained, olefin polymer slurries in a diluent are generally limited to no more than 37 to 40 weight percent solids. Hence settling legs have been believed to be necessary to give a final slurry product at the exit to the settling legs of greater than 37-40 percent. This is because, as the name implies, settling occurs in the legs to thus increase the solids concentration of the slurry finally recovered as product slurry.

SUMM [0008] It is a further object of this invention to operate a

- slurry olefin polymerization process in a diluent at a reactor solids concentration high enough to make direct continuous product takeoff commercially viable;
- SUMM [0009] It is a further object of this invention to operate a slurry olefin polymerization process in a diluent at higher circulation velocities.
- SUMM [0010] It is yet a further object of this invention to operate a slurry olefin polymerization process in a diluent in a reaction zone of greater than 30,000 gallons; and
- SUMM [0011] It is still yet a further object of this invention to provide a loop reactor apparatus having a capacity of greater than 30,000 gallons and having a continuous take off means.
- SUMM [0013] In accordance with another aspect of this invention, a loop reactor olefin polymerization process is carried out by operating at a higher circulation velocity for a given reactor pipe diameter.
- DRWD [0016] FIG. 1 is a schematic perspective view of a loop reactor and polymer recovery system;
- DRWD [0020] FIG. 5 is a side view of an elbow of the loop reactor showing both a settling let and continuous take off assemblies;
- DETD [0026] Surprisingly, it has been found that continuous take off of product slurry in an olefin polymerization reaction carried out in a loop reactor in the presence of an inert diluent allows operation of the reactor at a much higher solids concentration. Commercial production of predominantly ethylene polymers in isobutane diluent has generally been limited to a maximum solids concentration in the reactor of 37-40 weight percent. However, the continuous take off has been found to allow significant increases in solids concentration. Furthermore, the continuous take off itself brings about some additional increase in solids content as compared with the content in the reactor from which it takes off product because of the placement of the continuous take off appendage which selectively removes a slurry from a stratum where the solids are more concentrated. Hence concentrations of greater than 40 weight percent are possible in accordance with this invention.
- DETD [0030] The present invention is applicable to any olefin polymerization in a loop reactor utilizing a diluent so as to produce a product slurry of polymer and diluent. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The invention is particularly suitable for the homopolymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.01 to 10, preferably 0.01 to 5, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer.
- DETD [0033] Referring now to the drawings, there is shown in FIG. 1 a loop reactor 10 having vertical segments 12, upper horizontal segments 14 and lower horizontal segments 16. These upper and

lower horizontal segments define upper and lower zones of horizontal flow. The reactor is cooled, my means of two pipe heat exchangers formed by pipe 12 and jacket 18. Each segment is connected to the next segment by a smooth bend or elbow 20 thus providing a continuous flow path substantially free from internal obstructions. The polymerization mixture is circulated by means of impeller 22 (shown in FIG. 8) driven by motor 24. Monomer, comonomer, if any, and make up diluent are introduced via lines 26 and 28 respectively which can enter the reactor directly at one or a plurality of locations or can combine with condensed diluent recycle line 30 as shown. Catalyst is introduced via catalyst introduction means 32 which provides a zone (location) for catalyst introduction. The elongated hollow appendage for continuously taking off an intermediate product slurry is designated broadly by reference character 34. Continuous take off mechanism 34 is located in or adjacent to a downstream end of one of the lower horizontal reactor loop sections 16 and adjacent or on a connecting elbow 20.

- DETD [0034] The continuous take off appendage is shown at the downstream end of a lower horizontal segment of the loop reactor which is the preferred location. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. However, the continuous take off appendage can be located on any segment or any elbow.
- DETD [0041] As can be seen from the relative sizes, the continuous take off cylinders are much smaller than the conventional settling legs. Yet three 2-inch ID continuous take off appendages can remove as much product slurry as 14 8-inch ID settling legs. This is significant because with current large commercial loop reactors of 15,000-18000 gallon capacity, six eight inch settling legs are required. It is not desirable to increase the size of the settling legs because of the difficulty of making reliable valves for larger diameters. As noted previously, doubling the diameter of the pipe increases the volume four-fold and there simply in not enough room for four times as many settling legs to be easily positioned. Hence the invention makes feasible the operation of larger, more efficient reactors. Reactors of 30,000 gallons or greater are made possible by this invention. Generally the continuous take off cylinders will have a nominal internal diameter within the range of 1 inch to less than 8 inches. Preferably they will be about 2-3 inches internal diameter. [0048] Commercial pumps for utilities such as circulating the reactants DETD in a closed loop reactor are routinely tested by
- their manufacturers and the necessary pressures to avoid cavitation are easily and routinely determined.
- [0049] A four vertical leg polymerization reactor using a 26 inch DETD Lawrence Pumps Inc. pump impeller D51795/81-281 in a M51879/FAB casing was used to polymerize ethylene and hexene-1. This pump was compared with a 24 inch pump which gave less aggressive circulation (0.66 ft of pressure drop vs 0.98). This was then compared with the same more aggressive circulation and a continuous take off assembly of the type shown by reference character 34 of FIG. 5. The results are shown below.

DATA TABLE

26 in Pump +CTO

Description 24 in Pump 26 in Pump

Date of Operation Oct 4-9, 1994 May 24-28, 1995 Nov 15-18, 1996

Avg. Reactor Solids	39	45	53
Concentration, wt % Polymer Production Rate, mlbs/hr	40.1	40.7	39.9
Reactor Circulation Pump Power, kw	430	691	753
Circulation Pump Pressure Diff, psi	14.3	22.4	23.7
Circulation Pump Head, ft	61.8	92.5	92.4
Reactor Slurry Flow Rate, mGPM	39	46	45
Reactor Slurry Density,	0.534	0.558	0.592
Reactor Temperature, F Ethylene 4.9	215.6 4.43	218.3 3.67	217.0
Concentration, wt %			
Hexene-1	0.22	0.17	0.14
Concentration, wt %			
Reactor Heat Transfer Coefficient	270	262	241
Reactor Inside Diameter, inches	22.0625	22.0625	22.0625
Reactor Volume, gal Reactor Length, ft Pressure Drop per Foot	18700 941 0.066	18700 941 0.098	18700 941 0.098
of Reactor, ft/ft CLM What is claimed is:			

1. A polymerization process comprising: polymerizing, in a loop reaction zone, at least one olefin monomer in a liquid diluent to produce a first fluid slurry comprising liquid diluent and solid olefin polymer particles; maintaining in said first slurry in said zone a concentration of ethylene of at least 3.67 weight percent and an average concentration of solid olefin polymer particles of at least 40 weight percent; and

continuously withdrawing said first slurry comprising withdrawn liquid diluent and withdrawn solid polymer particles, as an intermediate product of said process.

CLM What is claimed is:

2. The process of claim 1, wherein said concentration of ethylene is at least 4.43 weight percent.

CLM What is claimed is:

3. The process of claim 1, wherein said concentration of ethylene is at least $4.9~\mathrm{weight}$ percent.

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L7 ANSWER 41 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2006:61382 USPAT2

TITLE: Process and apparatus for producing olefin polymers

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corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION: APPLICATION INFO.:	US 7115687 WO 2004039847 US 2003-532607 WO 2003-FI799	B2	20061003 20040513 20031027 20031027 20050425	(10) PCT 371 date

NUMBER DATE

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PRIMARY EXAMINER: Teskin, Fred

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NUMBER OF CLAIMS: 20 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)

LINE COUNT: 569

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

The present invention concerns a process and an apparatus for continuous polymerisation of olefin monomers in a cascade of polymerisation reactors. According to the process, an olefin monomer is polymerised first in slurry phase in an inert hydrocarbon diluent in at least one loop reactor and then, subsequently, in gas phase in at least one gas phase reactor. According to the invention, a polymer slurry is continuously withdrawn from the loop reactor and optionally concentrated. The concentrated slurry is conducted to a high pressure flash unit in order to remove the remaining fluid phase, and fed to the gas phase reactor. With the process described in this invention, it is possible to produce bimodal polyethylene with good properties. The operation of the process is stable because of the truly continuous operation.

The present invention relates to olefin polymerisation. In particular, the present invention concerns a process and an apparatus for continuous polymerisation olefin monomers like ethylene and other monomers in a cascade of polymerisation reactors, wherein an olefin monomer is polymerised first in slurry phase in an inert hydrocarbon diluent in at least one loop reactor and then, subsequently, in gas phase in at least one gas phase reactor.

The loop reactor was developed in the 1950's. It is now widely used for the production of polyethylene and other olefin polymers. In a loop reactor, ethylene is polymerised in the presence of a hydrocarbon diluent in slurry phase at elevated pressure and temperature. The slurry is withdrawn from the reactor and concentrated so that the solids content at the reactor outlet is higher than the solids content in the reactor. Traditionally, this has been done by using settling legs. However, present methods for concentrating the polymer slurry of a loop reactor have been unsatisfactory. This is true, in particular, for the production of bimodal polyethylene in cascaded reactors.

SUMM The use of hydrocyclones for concentrating the outlet slurry of a loop reactor is known since the 1960's. Loop reactors equipped with a hydrocyclone are disclosed in, e.g.,

- U.S. Pat. No. 3,816,383, where a part of the underflow from the hydrocyclone is taken to product recovery, while the residual part is combined with the overflow and returned to the loop reactor.
- Another document relating to the above-mentioned topic is U.S. Pat. No. 4,395,523, which discloses a method of making and recovering polymer particles. The known method comprises polymerising in a loop reactor, directing a portion of the recirculating polymer slurry into a hydrocyclone, returning the overflow from the hydrocyclone into the reactor and withdrawing the underflow from the hydrocyclone and conducting it to product recovery.
- SUMM Further, EP 1 118 624, EP 1 118 625 and EP 1 118 626 disclose a process for polymerising olefins, where the polymer slurry is directed from a loop reactor into a hydrocyclone. The underflow from the hydrocyclone is directed either to a subsequent polymerisation stage or to product recovery.
- SUMM EP 891 990 discloses an ethylene polymerisation process comprising a continuous take-off of polymer slurry. The polymer slurry is continuously withdrawn from the loop reactor and fed to a high-pressure flash. From the high-pressure flash, the polymer is transferred into a low-pressure flash and from there to product recovery.
- SUMM EP 517 868 discloses a process for producing ethylene polymers in a reactor cascade comprising a loop reactor and a gas phase reactor. The document does not disclose how the polymer slurry is withdrawn from the loop reactor. Hydrocarbons are separated from the polymer, but no details are given on how this is done. Finally, the polymer is fed into the gas phase reactor.
- SUMM Even if the above documents describe different methods of withdrawing the slurry from the loop reactor, none of them discloses or suggests a suitable, cost efficient process for polymerising ethylene in two successive stages, the first stage being conducted in a loop reactor and the second stage in a gas phase reactor. The polymer is separated from the reaction mixture after the loop polymerisation stage and at least a part of the hydrocarbon mixture is removed. Then essentially no hydrogen is carried over to the gas-phase polymerisation reactor.
- SUMM The process of EP 517 868 comprises a low-pressure flash after the loop reactor for separating the polymer from the reaction mixture. While this provides effective separation, it is a relatively expensive process, because the overhead flow from the flash needs to be compressed before it can be returned into the loop reactor and the polymer must be fed into the gas phase reactor with e.g. a pressurising/depressurising sequence.
- One way of overcoming the above-mentioned problem involving the necessity of compressing the overhead flow from the flash, would be to replace the low-pressure flash of EP 517 868 with a high-pressure flash, as suggested in EP 891 990. However, if the slurry were withdrawn from the reactor continuously, as proposed in EP 891 990, the separation of the reactants would not be sufficiently efficient and, in particular, some hydrogen would be carried over from the loop reactor to the gas phase reactor, thus limiting the molecular

weight that could be produced in the gas phase reactor. The use of a combination of a high-pressure flash and a low-pressure flash would result in an expensive process. Finally, if the polymer slurry were withdrawn from the loop reactor intermittently by using settling legs and the thus withdrawn concentrated slurry would be conducted to a high-pressure flash, there would still remain the problem with high hydrogen concentration in the gas. However, the flash would now have to be designed for a high flow, because the flow rates are high at the times when the settling legs open to discharge the slurry. This overdesign and use of settling legs leads to a high investment cost.

- SUMM It is an aim of the present invention to eliminate the problems of the prior art and to provide a novel way of polymerising ethylene and other olefin monomers, optionally in the presence of comonomers, in a reactor cascade comprising a loop reactor and a gas phase reactor.
- SUMM It is a particular aim of the present invention to find an economical alternative to the process known from EP 517 868 by providing a novel and cost-efficient process for polymerising ethylene in two successive stages, the first stage being conducted in a loop reactor and the second stage in a gas phase reactor, where the polymer is separated from the reaction mixture after the loop polymerisation stage so that no reactant, especially no hydrogen, is transferred from the loop reactor to the gas phase reactor in such an extent that it would have an adverse effect in the polymerisation in gas phase.
- SUMM The invention is based on the idea of using, in combination, means located outside the loop reactor for increasing the solids content of the slurry withdrawn from the loop reactor to provide a concentrated slurry, and a high-pressure flash unit for essentially evaporating all of the remaining liquid-phase hydrocarbons of the slurry phase diluent to provide a gas/solids mixture containing polymer solids gases. Alternatively, the slurry can be concentrated when it is withdrawn from the reactor.
- SUMM Thus, the apparatus for producing an olefin polymer in the presence of a catalytic system preferably comprises, in a cascade, a loop reactor, means for increasing the concentration of polymer slurry withdrawn from the loop reactor, a high-pressure flash and a gas phase reactor. The means for increasing the concentration of the slurry can be located externally to the loop reactor or be arranged in conjunction with the reactor outlet.
- SUMM The process according to the invention for producing olefin polymers in the presence of a catalytic system in a continuously operated multistage polymerisation sequence, comprises the steps of
- continuously withdrawing from the loop reactor a polymer
 slurry containing polymer and a fluid mixture containing diluent,
 monomers and optionally hydrogen,
- optionally, concentrating the slurry by removing a part of the hydrocarbon diluent to provide a concentrated slurry,
- conducting the concentrated slurry to a high pressure flash unit in order to remove essentially all of the remaining hydrocarbon diluent and to provide a product stream containing a mixture of polymer solids and gases,

transferring the product stream from the flash into the gas phase reactor.

- DETD The reference numerals used in the attached drawing refer to the following pieces of equipment:
- 1. loop reactor
- 2. hydrocyclone
- 3. high pressure flash receiving vessel
- 4. gas phase reactor
- 11. loop reactor outlet line
- 21. overhead flow from the hydrocyclone
- 22. flash pipe (heated)
- 31. overhead flow to the diluent recycle
- 32. flow from the flash receiving vessel
- 33. polymer flow to the gas phase reactor
- 5. gas exchange zone
- DETD Olefin monomers like ethylene and optionally one or more alpha-olefin comonomer(s) are polymerised in a loop reactor 1 in a hydrocarbon diluent, preferably propane or isobutane, in the presence of a polymerisation catalyst, optionally in the presence of hydrogen. The polymer slurry is continuously withdrawn from the loop reactor 1 through an outlet nozzle.
- DETD At least a part of the polymer slurry thus withdrawn is conducted to a hydrocyclone 2, in which the slurry is concentrated to provide a first product stream having a high concentration of solid matter and a second product stream, which mainly consists of hydrocarbon diluent separated from the polymer slurry. The first product stream forms the underflow of the hydrocyclone 2 and it is conducted via flash pipe 22 to receiving vessel of the flash unit 3, which preferably is operated at a high pressure. The overhead flow comprising the second product stream of the hydrocyclone is recycled from the hydrocyclone 2 to the loop reactor 1.
- DETD At least a part of the overhead flow from the receiving vessel of the flash unit, consisting mainly of hydrocarbons is recycled directly or indirectly into the loop reactor 1 or gas phase reactor 4.
- DETD A. Loop Reactor
- DETD In the loop reactor 1, olefins like ethylene are homopolymerised or copolymerised with at least one C.sub.4 to C.sub.10 alpha-olefin. The polymerisation takes place in an inert hydrocarbon diluent or liquid monomer, preferably a C.sub.3 to C.sub.5 hydrocarbon diluent, more preferably in propane or isobutane diluent, and in particular propane diluent.
- DETD The temperature in the loop is from about 60° C. to about 110° C., preferably from 75 to 105° C. If ethylene or propylene is homopolymerised in the loop reactor, it is preferred to operate the loop reactor at conditions known as "supercritical", where the operating temperature exceeds the critical temperature of the reaction mixture and the operating pressure exceeds the critical pressure of the reaction mixture. At such conditions, the operation temperature is higher than 90° C., preferably higher than 93° C.
- DETD The operating pressure needs to be selected so that the contents of the loop reactor remain either in liquid state or supercritical state. For liquid slurry operation, the suitable range of operating pressure is from about 20 to about 100 bar, preferably from 25 to 75 bar. For supercritical slurry operation, the suitable range of operating pressure is from about 50 to about 100 bar, preferably from 55 to 80 bar.
- DETD Preferably, ethylene is (co)polymerised in the loop

reactor in the presence of hydrogen to produce the low molecular weight polymer component. Typically, the reaction mixture contains from 0 to 10%, preferably from 0 to 4 mol-% of alpha-olefin comonomer. If a Ziegler-Natta catalyst is used, the reaction mixture typically contains from 2 to 10 mol-% hydrogen, preferably from 2 to 8 mol-%. If a single site catalyst is used, the reaction mixture typically contains from 0.01 to 1 mol-% hydrogen. Further, the reaction mixture contains typically from 1 to 10 mol-%, preferably from 3 to 10 mol-% ethylene. If a single site catalyst is used, then slightly lower ethylene concentration may be used. The reaction mixture further comprises the components of the diluent. Preferably, the major part of the diluent is propane, with minor quantities of other alkanes, such as methane, ethane, and butanes.

- DETD The polymer slurry is withdrawn from the loop reactor continuously through an outlet. The outlet may be placed at any suitable location in the reactor. However, most preferably the outlet is located at a suitable location downstream of the loop circulation pump. It is also possible to withdraw the slurry from the loop reactor in such a manner that the concentration of solids at the outlet is higher than the concentration of solids in the loop reactor. The slurry may be directed into the flash unit directly or through a further concentration step.
- DETD From the loop reactor 1 the polymer slurry is directed to a hydrocyclone 2, where the concentration of the slurry takes place by effect of centrifugal forces. The hydrocyclone divides the slurry flow into two streams: An overflow 21, which is rich in liquid, and an underflow, which is rich in polymer. The overflow is returned to the loop reactor or to a fines collection tank (not shown in the drawing) and the underflow is directed to a flash unit.
- DETD As described above, the slurry entering the hydrocyclone has a solids content of 10 to 40% by volume. The solids concentration in the underflow can be adjusted by adjusting the ratio of the recycle flow (overflow) to the product flow (underflow), and is typically from 30 to 55% by volume, preferably 40 to 52% by volume. It is often advantageous to recycle a part of the underflow back to the loop reactor.
- The flash unit 3 typically consists of a heated flash pipe 22 and a receiving vessel 3. The slurry entering the flash unit has a solids concentration of 30 to 60% by volume. In the flash unit, the remaining hydrocarbons are removed from the polymer. The flash pipe is preferably heated, e.g. by steam or water. If water is used for heating, the heating water can be advantageously taken from the jacket of the loop reactor. The temperature is selected according to the composition of the hydrocarbon fluid so that the fluid is essentially evaporated. The phrase "essentially removing the fluid phase" means that a major fraction of the fluid phase is removed and only an amount of fluid that fills the volume between the polymer particles and the volume of pores in the polymer particles remains with the polymer. Typically, the temperature at the receiving vessel is from 50 to 100° C., preferably from 60 to 90° C., in particular from 70 to 90° C., and a pressure of 10 to 30 bar, preferably 12 to 27 bar, and in particular from 14 to 24 bar. The pressure is preferably higher than the pressure in the gas phase reactor, to allow smooth transfer of the polymer into the gas phase reactor. Advantageously, the pressure is at least 0.05 bar higher than in the gas phase reactor.
- DETD At least a part of the overhead flow 31 from the receiving vessel of the flash unit 3 is passed to the recovery system for recycling into the

loop reactor 1 or gas phase reactor 4 or both. A small purge stream can be recycled e.g. to a cracker.

- DETD The product flow 32 from the flash receiving vessel 3 is directed into a gas phase reactor. The flow contains about the void volume of gas of the same composition as the loop reactor fluid the rest being polymer. Before introduction into the gas phase reactor, the product flow can be passed through a gas exchange zone 5, where it is flushed countercurrently with essentially hydrogen free gas fraction from the diluent recovery or with a pure hydrocarbon, preferably propane, to reduce the amount of hydrogen carryover to the gas phase reactor. The gas displacement zone comprises a conduit and a control valve or optionally one or two rotary feeders.
- Summarising what has been stated above, one particularly preferred embodiment of the invention comprises the following steps: Polymerising the monomer in the presence of a catalytic system in a loop reactor 1 using a suitable catalyst and an inert hydrocarbon diluent, continuously withdrawing the polymer slurry from the loop reactor through an outlet line 11, concentrating the slurry in a hydrocyclone 2 to remove excess hydrocarbons to provide a concentrated slurry, returning the overflow 21 containing hydrocarbons from the hydrocyclone to the loop reactor, directing the concentrated slurry through a heated flash pipe 22 to the receiving vessel 3 of the high pressure flash unit in order to remove excess fluid reaction mixture, directing the product flow 32 from the receiving vessel of the flash unit into a gas phase reactor.
- DETD A 20 m.sup.3 loop reactor is operated at 95° C. and 60 bar pressure with propane diluent. Ethylene homopolymer is produced in the reactor by introducing ethylene, diluent, hydrogen and a polymerisation catalyst, which was prepared according to Example 3 of EP 688 794 with the exception that as a carrier material silica having an average particle size of 20 µm is used, in such quantities that the diluent contains 5.9 mol-% of ethylene and 2.6 mol-% hydrogen. The remainder is propane with minor quantities (less than 1 mol-% each) of methane, ethane, isobutane and n-butane. The polymer production is 2.8 tons per hour; the melt index of the polymer is 450 g/10 min and the density 973 kg/m.sup.3. The solids content of the slurry is 25 vol-%.
- DETD The polymer slurry is withdrawn continuously from the reactor through an outlet nozzle and transferred to a hydrocyclone according to FIG. 1. The total slurry feed to the hydrocyclone is 5.5 tons per hour. The product flow is 3.7 tons per hour, with 52 vol-% of solids. The recycle flow is 1.8 tons per hour, with 1.7 vol-% solids. The recycle flow is returned to the loop reactor.
- DETD The product flow of the hydrocyclone is routed into a flash pipe and further to a flash receiving vessel, operated at a temperature of 75° C. and a pressure of 21 bar. The hydrocarbons separated from the polymer are returned into the loop reactor via a diluent recovery. They contain 5.9 mol-% of ethylene and 2.6 mol-% of hydrogen.
- DETD The polymer slurry is withdrawn continuously from the reactor through an outlet nozzle and transferred to a hydrocyclone according to FIG. 1. The total slurry feed to the hydrocyclone is 5.2 tons per hour. The product flow is 3.8 tons per hour, with 39 vol-% of solids. The recycle flow is 1.4 tons per hour, with 5.8 vol-% solids. The recycle flow is returned to the loop reactor.
- DETD The product flow of the hydrocyclone is introduced into a flash pipe and further to a flash receiving vessel, operated at a temperature of 80° C. and a pressure of 20 bar. The hydrocarbons separated from the polymer are returned into the loop reactor. They contain 5.9 mol-% of ethylene, 3.7 mol-% 1-butene and 2.6

mol-% of hydrogen.

CLMWhat is claimed is:

> 1. A process for producing olefin polymers in the presence of a catalytic system in a continuously operated multistage polymerisation sequence, wherein an olefin monomer is polymerised first in slurry phase in a hydrocarbon diluent or liquid monomer, in at least one loop reactor, the slurry having a first concentration of solids, and then subsequently in gas phase in at least one gas phase reactor, said process comprising continuously withdrawing from the loop reactor a polymer slurry containing polymer and a fluid phase, further containing hydrocarbons and optionally hydrogen, concentrating the slurry by removing a part of the fluid phase to provide a concentrated slurry, conducting the concentrated slurry having a second concentration of solids, which is higher than the first concentration of solids, to a high pressure flash unit in order to remove essentially all of the remaining fluid phase and to provide a product flow containing a suspension of polymer solids and gases, and feeding the product flow of the flash unit into the gas phase reactor, wherein a receiving vessel of the flash unit is operated at a pressure of 10 to 30 bar, the operating pressure of the flash unit being higher than the pressure in the gas phase reactor.

CLM What is claimed is:

5. The process according to claim 1, wherein the slurry is withdrawn from the loop reactor in such a manner that the concentration of solids at the outlet is higher than the concentration of solids in the loop reactor.

What is claimed is: CLM

> 6. The process according to claim 4, wherein the overflow is recycled to the loop reactor.

CLM What is claimed is:

> 13. The process according to claim 12, wherein the flash pipe is heated with water taken from a jacket of the loop reactor.

CLM What is claimed is:

> 14. The process according to any of claims 11 to 13, wherein the overflow from the flash is recycled into the loop reactor or conducted to the gas phase reactor or both.

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ANSWER 42 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:248259 USPAT2

Cascaded polyolefin slurry TITLE:

polymerization employing disengagement vessel

between reactors

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NUMBER KIND DATE

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DOCUMENT TYPE: Utility FILE SEGMENT: GRANTED PRIMARY EXAMINER: Teskin, Fred GRANTED

LEGAL REPRESENTATIVE: Brooks Kushman P.C.

NUMBER OF CLAIMS: 18 EXEMPLARY CLAIM:

NUMBER OF DRAWINGS: 3 Drawing Figure(s); 2 Drawing Page(s)

LINE COUNT: 650

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

ΤI Cascaded polyolefin slurry polymerization employing disengagement vessel between reactors

AΒ A disengagement vessel employing a lock hopper effectively reduces concentration of non-polymer-associated components in the polymer product slurry of a first olefin slurry polymerization reactor, allowing cascading of a second slurry polymerization reactor operating at lesser concentration of comonomers, hydrogen, and other components to produce multicompositional polyolefin polymers and/or polymers having a multimodal monomer distribution, e.g. diblock polymers having substantially non-overlapping comonomer contents between the blocks.

SUMM The present invention pertains to the use of cascaded slurry reactors to polymerize olefins to produce polyolefin homo- and copolymers of multimodal molecular weight distribution and/or composition.

SUMM Slurry reactors are in widespread use for production of polyethylene homo- and copolymers. Slurry reactors include stirred tank reactors and water-jacketed tubular reactors arranged in a series of continuous horizontal or vertical loops. A "slurry solvent" in which polyethylene has low solubility constitutes the continuous phase in such reactors, and in the case of slurry loop reactors, is driven around the loop at relatively high speed by one or more rather massive pumps. Ethylene, supported catalyst, comonomers, and processing additives are injected into the loop where polymerization takes place, creating a slurry of polyethylene in solvent. A plurality of settling legs allow polymer particles to partially sediment out, creating a slurry of higher solids content, which is released periodically to harvest polymer. Slurry processes are widely used throughout the world. It has recently been proposed to cascade slurry reactors to produce multimodal resins.

U.S. Pat. Nos. 6,221,982 B1 and 6,291,601 B1 disclose cascaded SUMM slurry polymerizations where at least two distinct catalysts are employed. In U.S. Pat. No. 6,221,982, a Ziegler-Natta catalyst is employed in the first reactor with high hydrogen concentration and no or low comonomer incorporation. A hydrogen-consuming catalyst with low olefin polymerization efficiency is introduced downstream into the first reactor product stream. As a result, hydrogen is consumed prior to reaching the second reactor, wherein the polymerization is conducted at substantially zero hydrogen concentration. The second stage employs significant olefin comonomer. U.S. Pat. No. 6,291,601 is similar, but employs a metallocene catalyst in the first reactor.

SUMM U.S. Pat. No. 6,225,421 B1 discloses use of cascaded reactors wherein ethylene is homopolymerized in the presence of hydrogen in a first reactor, hydrogen is physically separated from the first reactor product stream, and the product is copolymerized with 1-hexene and additional

ethylene at reduced hydrogen concentration in the second reactor. However, the patent contains no disclosure of any apparatus suitable for removing hydrogen from the first reactor product stream. Moreover, the necessity to restrict the first polymerization to homopolymerization is limiting.

- It has now been surprisingly discovered that hydrogen and other SUMM components which are not associated with polyolefin particles may be effectively removed from the product stream of a first polyolefin slurry polymerization reactor through means of a disengagement vessel equipped with a lock hopper for harvesting a polyolefin polymer slurry having significantly reduced concentration of "non-polymer-associated components." The process preferably removes hydrogen from the first slurry reactor. The lock hopper contents are flushed intermittently into a subsequent polymerization reactor.
- Slurry processes for olefin polymerization are well DETD known, and are described, for example, in PROCESS ECONOMICS PROGRAM REPORTS 185 and 185A (2000). Additional details may be found in the patents cited previously, herein incorporated by reference, and in many other patents, publications and treatises. These and other references also disclose numerous catalysts, modifiers, etc., which can be used in slurry polymerization processes.
- DETD In a preferred embodiment of the present invention, the hydrogen content of a first reactor product stream is lowered to a lower concentration by means of a disengagement vessel ("DV") for hydrogen ("HDV"), generally of elongate construction, equipped with a lock hopper for product transfer at a lower end thereof. The remaining details of the slurry polymerization process are conventional and well known to those skilled in the art.
- DETD FIG. 2 illustrates a simplified diagram of a cascaded polyolefin slurry polymerization process employing a disengagement vessel of the subject invention. FIG. 2 illustrates two continuous loop slurry reactors 30 and 31. The first slurry loop reaction is shown with three feed lines 34, 35 and 36, although a greater or lesser number may also be used. These feed lines feed solvent, monomer, comonomer (when used), hydrogen, catalyst, catalyst activators and water scavengers, antistats, etc., either with dedicated inlets for each, or combination inlets. From one loop of slurry loop reactor legs, a product takeoff leg 38, which may be of the continuous type, or a single or one of a plurality of conventional settling legs, provides a polymer slurry from reactor 30 to the hydrogen disengagement vessel 40 as previously described. Fresh solvent is optionally added to the product takeoff leg at 41, while gases exit the DV at 43. Hydrogen disengagement is augmented by a nitrogen inlet (sparge) 44, and settling polymer particles collect in the lower portion 45 of DV 40, and flow intermittently into solvent-filled lock hopper 50. The polymer is flushed intermittently from the lock hopper by opening and then closing flush valves 52 and 53, valve 52 flushing the polymer from the lock hopper through valve 53 by means of fresh solvent 51. The outlet slurry flowing through line 54 serves as an inlet stream to subsequent reactor 31, along with additional inlet streams 55, 57 and 58, which, for example, may feed additional olefin monomer, comonomer, and solvent, and optionally but not preferredly, additional catalyst, activator, scavengers, and the like. Product takeoff from reactor 31 is preferably by means of one or more conventional settling legs 60. The product slurry is treated conventionally to remove solvent and unreacted monomers, i.e., by a series of product separation flash drums. DETD
- A pilot plant cascaded reactor configuration is employed to produce

polyethylene copolymers. The first reactor is a slurry loop reactor having a volume of 44 gallons (166 L), while the second reactor is an 88 gallon (232 L) slurry loop reactor. The settling leg of the first reactor is directed to a 170 gallon (643 L) disengagement vessel as shown in FIG. 1. The lock hopper of the disengagement vessel is that of FIG. 3. The overall process is therefore similar to that shown in FIG. 2.

CLM What is claimed is:

1. A process for disengagement of non-polymer-associated components from a first slurry polymerization reactor product slurry stream containing solid polymer particles in a slurry solvent, said method comprising: introducing a non-polymer-associated component-containing polymer slurry from a first slurry reactor into a disengagement vessel, said disengagement vessel terminating at a lower end thereof with a lock hopper having a cavity therein which is selectively communicatable between an interior of said disengagement vessel and a supply of slurry solvent; filling said cavity with slurry solvent when said cavity is not in fluid communication with said disengagement vessel; causing said cavity to be in fluid communication with said interior of said disengagement vessel, and allowing polymer particles contained in a polymer particle slurry in said disengagement vessel to enter said cavity, displacing slurry solvent into said disengagement vessel from said cavity; ceasing communication of said cavity with said interior of said disengagement vessel, establishing fluid communication of said cavity with said supply of slurry solvent, and flushing polymer particles from said cavity with slurry solvent as a solvent flush polymer slurry, at least one non-polymer-associated component concentration in said solvent flush polymer slurry being less than the concentration of said at least one non-polymer-associated component in said disengagement vessel.

CLM What is claimed is:

4. The process of claim 1, wherein said non-polymer-associated component-containing polymer slurry is collected in a settling leg of said first slurry reactor at a higher polymer solids content than the polymer content of the polymer slurry circulating in the first slurry polymerization reactor, and is diluted with additional solvent prior to entering said disengagement vessel.

CLM What is claimed is:

10. A process for the slurry polymerization of an olefin monomer and optionally of unsaturated comonomers to form a polyolefin polymer having a multimodal molecular weight distribution, employing the disengagement method of claim 1, said process comprising: a) introducing olefin monomers, slurry solvent, and optionally unsaturated comonomers, hydrogen, and at least one olefin polymerization catalyst into a first slurry polymerization reactor, and polymerizing to form a first polymer particle slurry; b) withdrawing a first polymer particle slurry containing at least one non-polymer-associated component from said first slurry polymerization reactor and introducing said first polymer particle slurry into a disengagement vessel having a lock hopper proximate the bottom thereof, said lock hopper having a cavity selectively communicable with an interior of said disengagement vessel and a slurry solvent supply; c) filling said lock hopper cavity with slurry solvent to form a slurry solvent-containing lock hopper cavity; d) establishing communication of said slurry solvent-containing lock hopper cavity with said interior of said disengagement vessel, whereby polymer particles enter said cavity, displacing slurry solvent therefrom into the interior of said disengagement vessel, to form a slurry

solvent-washed polymer slurry in said cavity; e) terminating communication of said cavity with said interior of said disengagement vessel, flushing said slurry solvent-washed polymer slurry from said cavity with slurry solvent as a solvent flush polymer slurry, and refilling said cavity with slurry solvent; f) introducing said solvent flush polymer slurry into a subsequent slurry polymerization reactor; q) introducing a polymerization mixture comprising further olefin monomer, optionally unsaturated comonomer(s), optionally hydrogen, and optionally further olefin polymerization catalyst into said subsequent slurry polymerization reactor, the concentration of at least one non-polymer-associated component in said subsequent polymerization reactor being less than the concentration of at least one non-polymer-associated component in said first slurry polymerization reactor; and h) recovering from said subsequent slurry polymerization reactor a polyolefin polymer having a multimodal molecular weight distribution, a multicompositional monomer distribution, or both a multicompositional molecular weight distribution and a multimodal monomer distribution.

CLM What is claimed is:

11. The process of claim 10, wherein three slurry polymerization reactors are employed, an intermediate slurry reactor preceding said subsequent slurry polymerization reactor, and at least one disengagement vessel to lower concentration of at least one non-polymer-associated component, said at least one disengagement vessel located between any two of said three slurry reactors.

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L7 ANSWER 43 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:159383 USPAT2

ACCESSION NOMBER: 2004:139303 USFAI2

TITLE: Continuous withdrawal from high solids slurry

polymerization

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NUMBER OF DRAWINGS: 9 Drawing Figure(s); 7 Drawing Page(s)

LINE COUNT: 682

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Continuous withdrawal from high solids slurry polymerization

SUMM The present invention relates to the slurry polymerization of olefin monomers. More particularly, the present invention relates to improved techniques for continuously withdrawing a portion of the fluid slurry from a loop reaction zone and operating a loop reactor having a plurality of continuous take off.

SUMM Polyolefins such as polyethylene and polypropylene may be prepared by particle form polymerization, also referred to as slurry polymerization. In this technique, feed materials such as diluent, monomer and catalyst are introduced to a loop reaction zone, and a fluid slurry containing solid polyolefin particles in a liquid medium (usually an inert diluent and/or unreacted monomer) is circulated through the loop reaction zone. A portion of the fluid slurry is withdrawn from or taken off the reaction zone so that the solid polyolefin particles can be recovered.

SUMM In continuous loop reactors, the various feed materials may be introduced to the loop reaction zone in various ways. For example, the monomer and catalyst may be mixed with varying amounts of diluent prior to introduction to the loop reaction zone. The monomer may also be combined with recycled diluent and then fed to the loop reaction zone. In the loop reaction zone, the monomer and catalyst become dispersed in the fluid slurry. As the fluid slurry circulates through the loop reaction zone, the monomer reacts at the catalyst in a polymerization reaction. The polymerization reaction yields solid polyolefin particles in the fluid slurry.

SUMM Slurry polymerization in a loop reaction zone has proven commercially successful. The slurry polymerization technique has enjoyed international success with billions of pounds of olefin polymers being so produced annually. With this success has come the desirability, in some situations, of building larger reactors. Larger reactors lead to higher flow rates of fluid slurry. The flow rate inside a loop reactor can be as high as 1,000,000 gallons (3,785,410 liters) per minute or more.

Flow restriction causes loss of flow through the take off valve and may cause more polymer particles to build up. This may cause the reactor pressure to increase, since it is usually controlled (at least partially) by how much the take off valve is opened. If the build up in polymer particles is quicker than the action of the control mechanism for controlling pressure by opening the take off valve, a plugged line and excessive reactor pressures may result. This may be especially severe for fused or atypical polymer chunks that can grow in the loop reactor and have a much larger dimension than the largest polymer particle size. Plugged reactor take off valves can lead to reactor over pressure, downtime, production loss, and in extreme situations, relief of reactor pressure by process safety relief valves.

- As another aspect, a loop reactor apparatus is SUMM provided. The loop reactor apparatus includes a plurality of major segments and a plurality of minor segments. Each of the major segments is connected at a first end to one of the minor segments, and is connected at a second end to another minor segment. As a result, the major segments and the minor segments form a continuous flow path adapted to convey a fluid slurry. The continuous flow path is substantially free from internal obstructions. The loop reactor also includes a means for introducing an olefin monomer and/or a liquid medium (for example, an inert diluent) into the continuous flow path, a means for introducing a polymerization catalyst into the continuous flow path, and at least two means for continuously taking off a portion of the fluid slurry from the continuous flow path. Alternatively, the loop reactor includes at least four means for continuously taking off a portion of the fluid slurry. Such a loop reactor may have a volume greater than 30,000 gallons, alternatively greater than 35,000 gallons, alternatively greater than 40,000 gallons, alternatively greater than 45,000 gallons, alternatively greater than 50,000 gallons, alternatively greater than 75,000 gallons, alternatively greater than 100,000 gallons.
- SUMM As yet another aspect, a loop reactor apparatus is provided. The loop reactor apparatus comprises a plurality of major legs and a plurality of minor segments. Each minor segment connects two of the major legs to each other, and by these connections, the legs and the segments comprise a continuous flow path. A monomer feed is attached to one of the legs or segments. At least one catalyst feed is attached to one of the legs or segments. A continuous take off is attached to one of the legs or segments. The continuous take off includes a slurry withdrawal line in fluid communication with the reactor, a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line, and a flush line fluidly connected to provide diluent to the slurry withdrawal line.
- SUMM In the foregoing loop reactor apparatus, at least two of the minor segments form continual curves. At least two of the continual curves have one or more continuous take off mechanisms or means attached to them. The loop reactor apparatus may be essentially free of horizontal flow paths in that all the major legs are connected by continual curves.
- The apparatus may also include at least one spare continuous take off mechanism or means for continuously withdrawing product slurry. Preferably, the continuous take off mechanism or means comprises a V-ball valve having a nominal body size of at least 11/2 inch. The continuous take off valve may be automatically controlled by a controller, which adjusts the continuous take off valve in response to one or more input signals from pressure transmitters on the monomer feed to the loop reactor (or other means for introducing the olefin monomer to the loop reactor).

 Additionally or alternatively, a pressure transmitter may be disposed on the slurry withdrawal line downstream of the continuous take off valve. The pressure transmitter may be operatively connected to provide a signal to the controller. One or all of the continuous take off mechanisms or means may be automatically controlled in such fashions.
- SUMM As yet another aspect, a continuous take off mechanism for a loop polymerization reactor is provided. The mechanism comprises a slurry withdrawal line in fluid communication with the

reactor, a take off valve disposed along the slurry withdrawal line for regulating flow of the slurry through the slurry withdrawal line, a flush line fluidly connected to provide diluent to the slurry withdrawal line, and a controller. The controller is configured to receive an input signal from pressure transmitters disposed on a monomer feed and on the slurry withdrawal line downstream of the take off valve. The controller is also configured to send an output signal to adjust the take off valve.

- SUMM As yet another aspect, a process for starting a loop polymerization reactor is provided. The process comprises feeding ethylene to the reactor and feeding isobutane to the reactor. The mass ratio of ethylene to isobutane fed to the reactor is sufficiently low to avoid plugging of the continuous take off mechanism.
- As still another aspect, a process for operating a loop polymerization reactor is provided. The process includes feeding ethylene to the reactor, feeding isobutane to the reactor, feeding a polymerization catalyst to the reactor, circulating a fluid slurry comprising unreacted ethylene and solid polyethylene particles in the isobutane through the reactor, continuously withdrawing a portion of the fluid slurry through a plurality of continuous take off mechanisms, and continuously flushing isobutane through the slurry withdrawal line of an inactive continuous take off mechanism. In this manner, a "hot spare" or "hot standby" is provided for the reactor.
- DRWD FIGS. 1(a) and (b) show loop reactors and polymer recovery systems.
- DRWD FIG. 5 is a side view of an elbow of the loop reactor showing a continuous take off mechanism.
- DRWD FIG. 7 is a side view of an elbow of the loop reactor showing the placement of a plurality of continuous take off mechanisms.
- DRWD FIG. 8 is a cross section of a portion of a loop reactor and two continuous take off mechanisms.

polyethylene herein.

- DETD The present process and apparatus relate to continuous take off or withdrawal of a portion of the fluid slurry in a loop reactor. This facilitates operation of the loop reactor at a much higher solids concentration

 . In particular, the present process and apparatus relate especially to
 - large loop reactors having continuous take off instead of settling legs. The present techniques facilitate reliable operation of such large reactors and reliable withdrawal of product.
- The present process and apparatus are applicable to any olefin DETD polymerization in a loop reactor that produces a slurry of solid polyolefin particles in a liquid medium. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The present process and apparatus are particularly suitable for the homo polymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.1 to 10 weight percent, preferably 0.01 to 5 weight percent, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer. Such polymers are still referred to as

- DETD Additional details regarding loop reactor apparatus and polymerization processes may be found in U.S. Pat. Nos. 4,674,290; 5,183,866; 5,565,174; 5,624,877; 6,005,061; 6,045,661; 6,051,631; 6,114,501; and 6,420,497, which are also incorporated by reference herein.
- Referring now to the drawings, FIG. 1(a) shows a loop DETD reactor 10 having eight vertical segments 12, upper horizontal segments 14 and lower horizontal segments 16. The horizontal segments may be replaced by curved segments or continual curves so that the reactor contains essentially no horizontal flow paths, as shown in FIG. 1(b). In FIG. 1(a), these upper and lower horizontal segments define upper and lower zones of horizontal flow. In FIG. 1(b), the upper and lower curved segments 14a and 16a take the places of the horizontal segments. The reactor is cooled by means of heat exchangers formed by pipe 12 and jacket 18. Each segment is connected to the next segment by a smooth bend or elbow 20 thus providing a continuous flow path substantially free from internal obstructions. The fluid slurry is circulated by means of an impeller driven by motor 24. Monomer (and comonomer, if any) and fresh diluent are introduced through lines 26 and 28 respectively which can enter the reactor directly at one (as shown in FIG. 1(a)) or a plurality (as shown in FIG. 1(b)) of locations or can combine with recycled diluent line 30 as shown. In FIG. 1(b) the recycle diluent line splits to provide four feed points 30a, 30b, 30c, and 30d. During initial start-up of a loop reactor having one or more continuous take off mechanisms, it has been found desirable to increase the amount of recycled diluent fed to the reactor, with respect to the ethylene fed to the reactor. For example, a 1:1 mass flow ratio of ethylene and recycled isobutane during initial start-up has been found to reduce plugging of the continuous take off mechanism. Smaller mass flow ratios, for example, 4:5 or 2:3, may also be used. Catalyst is introduced via catalyst introduction means 32 which provides a zone (location) for catalyst introduction.
- DETD A continuous take off mechanism for withdrawing an intermediate product slurry is designated broadly by reference character 34. Continuous take off mechanism 34 is located in or adjacent to an end, preferably a downstream end, of one of the lower horizontal segments 16 or the lower curved segments 16a or adjacent or on a connecting elbow 20. One advantage of the continuous take off mechanism 34 is that it can eliminate the need for horizontal segments. Settling legs typically were attached to horizontal segments. Using continuous take off mechanisms facilitates the use of preferable curved segments. The continuous take off mechanism 34 is shown at the downstream end of a lower horizontal segment of the loop reactor. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. It is presently preferred to locate a continuous take off at an upward flowing elbow (an elbow in which the fluid slurry turns upward to flow up a vertical segment). However, the continuous take off mechanism can be attached to any segment, elbow or curve.
- DETD As described in U.S. Pat. No. 6,239,235, polymerization processes utilizing continuous take off instead of a traditional settling leg for slurry take off are favored for larger reactors. U.S. Pat. No. 6,239,235 (which is incorporated herein by reference) discloses an olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and slurry is withdrawn by use of a continuous take off mechanism. The process may be employed in loop reaction zones of greater than 30,000 gallons. Also, reactor polymer solids concentrations of greater than 50 weight percent

DETD

are discussed.

DETD Vaporized diluent exits the high pressure flash chamber 38 through conduit 42 for further processing which includes condensation by simple heat exchange using recycle condenser 50, and return to the loop reactor, without the necessity for compression, via recycle diluent line 30. Recycle condenser 50 can utilize any suitable heat exchange fluid known in the art under any conditions known in the art. However preferably a fluid at a temperature that can be economically provided is used. A desirable temperature range for this fluid is 40 degrees F. to 130 degrees F. Polymer particles are withdrawn from high pressure flash chamber 38 via line 44 for further processing using techniques known in the art. The polymer particles may be passed to low pressure flash chamber 46 (or directly to a purge zone) and thereafter recovered as polymer product via line 48. Separated diluent passes through compressor 47 to line 42. This high pressure flash design is broadly disclosed in U.S. Pat. No. 4,424,341, which is hereby incorporated by reference.

DETD FIG. 2 shows a curved segment 16a with continuous take off mechanism 34 in more detail. The continuous take off mechanism typically at least includes a slurry withdrawal line in fluid communication with the reactor and a valve for controlling the flow of slurry through that line. The continuous take off mechanism shown in FIG. 2 comprises a take off cylinder 52 attached to the reactor with a flange 53, a slurry withdrawal line 54, an emergency shut off valve 55 (or block valve), a proportional motor valve 58 (the CTO valve) to regulate flow and a flush line 60. The cylinder 52 need not extend into the reactor; indeed, extending a protrusion into a loop slurry reactor may result in polymer build-up around the protrusion. However, in some circumstances the cylinder may extend into the reactor. Diluent input is generally held constant, the proportional motor valve 58 being used to control the rate of continuous withdrawal to maintain the total reactor pressure within designated set points. A manual flash line may also be connected with the flash line downstream of the proportioned motor valve 58. Diluent input may be adjusted based upon logic which calculates and controls the weight percent of solids in the reactor.

It has been found desirable to maintain at least one continuous take off mechanism in inactive status by closing block valve 66 (or another downstream valve) rather than ram valve 62. A continuous take off is inactive if it is not being used to withdraw product slurry as part of the normal commercial production of the polyolefin. The flush line 70 and flush valve 72 may also be operated to automatically feed diluent to slurry withdrawal line 54 if a downstream valve or block valve is shut or plugged. By closing block valve 66 or other downstream valve but leaving ram valve 62 open, the continuous take off mechanism can be maintained as a "hot spare" or "hot standby" that may rapidly, essentially instantaneously, remotely, and/or automatically be put into use if needed. By maintaining a "hot spare" continuous take off mechanism, an additional continuous take off mechanism can rapidly (within 1 minute or less) be put into operation during certain situations and prevent high pressure in the reactor. The continuous take off mechanism can be maintained as a hot spare by continually flushing diluent through flush line 70 and flush valve 72 when the block valve 66 is closed. Alternatively, a hot spare may have the block valve open and another downstream valve (for example, the proportional motor valve 58 or the CTO valve 74) closed. In that case, the flush line 70 and flush valve 72 may be locate downstream of block valve 66. The flush line 70 and flush valve 72 may also be operated to automatically feed diluent to slurry withdrawal line 54 if the continuous take off mechanism is shut or plugged. It is highly desirable to equip the loop reactor with at least one continuous take off mechanism to exist

as a spare, in case the active continuous take off mechanism become plugged, which is a significant risk during operation.

DETD In FIG. 4, an automatic control is shown in the form of a programmable controller 76, which adjusts the CTO valve 74 in response to one or more input signals. The input signals in FIG. 4 are from pressure transmitters 78 and 79 on feed lines 80 and 81 to the loop reactor. However, the input signal may be indicative of the pressure (or other parameter) in the reactor or in downstream equipment, such as the flash line or a flash chamber.

DETD The continuous take off cylinders are smaller than the conventional settling legs. Yet three 2-inch ID continuous take off appendages can remove as much product slurry as 14 eight-inch ID settling legs. This is significant because with commercial loop reactors of 15,000-18,000 gallon capacity, 6 eight-inch settling legs are required. It is not desirable to increase the size of the settling legs because of the difficulty of making reliable valves for larger diameters. Reactors of 30,000 gallons or more benefit from the present process and apparatus. Generally the continuous take off cylinders will have a nominal internal diameter within the range of from about 1 inch to about 8 inches. Preferably they will be from about 2 to about 3 inches internal diameter. As the line extends from the reactor, the diameter may gradually increase or decrease to provide the desired effect on pressure and/or flow within the line. The line may gradually reduce in diameter leading to the CTO valve (and gradually increase in diameter after passing the CTO valve) in order to adapt to the size of the control valve, maintain a high slurry velocity and/or not provide sharp edges that can lead to polymer buildup. For example, a 2 inch line diameter may gradually taper to 1.5 inch diameter over 3 inches before the CTO valve 74, and then reverse-taper from 1.5 inch diameter to 2 inch over a similar distance after the CTO valve 74. In FIG. 4, tapered conduits or swedges 86 and 88 are shown before and after the CTO valve 74. Nonetheless, it is important to ensure there are no sudden enlargements or contractions of the lines' diameters, as that could lead to plugging. Preferably, the housing of the CTO valve is flanged for attachment to hollow appendages through which the withdrawn slurry flows. For the same reason, it is important to ensure smooth connections between pipes and no misalignments between pipe connections.

DETD FIG. 7 is a side view of an elbow of the loop reactor showing the placement of a plurality of continuous take off mechanisms. Four continuous take off mechanisms are shown, though only two are active; the other two continuous take off mechanisms are provided as options or spares. In FIG. 7, the continuous take off 34d and 34e are located at curve angles 30 degrees and 60 degrees on the downward flow leg (that is, the leg through which the fluid slurry is flowing downward), and the continuous take off 34f and 34g at 70 degrees and 40 degrees on the upward flow leg (that is, the leg through which the fluid slurry is flowing upward). In general, ranges of 0-60 degrees on a downward flow leg and a range of 30-90 degrees, more preferably 70-90 degrees, on an upward flow leg are preferred.

DETD FIG. 8 shows a cross section of a horizontal segment of a loop reactor and two continuous take off mechanisms 34b and 34c.

These continuous take off mechanisms 34b and 34c are disposed along a horizontal segment of the loop reactor 10 and form angle gamma with the bottom edge of the horizontal segment. The angle gamma is greater than 0 degrees and less than or equal to 90 degrees. This arrangement is especially suitable for a horizontal loop reactor which does not have upward or downward flowing elbows. In other words, this arrangement is suitable for the horizontal loop reactor where the major segments and minor segments are all disposed in an essentially horizontal plane. The

horizontal segments need not extend along a perfectly horizontal axis but rather may be substantially horizontal. For example, a horizontal segment may be positioned at a tilt or angle that is between 0 and 15 degrees from a true horizontal plane.

DETD It has been discovered that automatic and/or regular movement of the continuous take off valve is useful for reducing or avoiding instances of plugging in the valve. Regular movement of the continuous take off valve may attain a reduction in instances of continuous take off valve plugging. The short localized pressure pulse created by the movement of the continuous take off valve can reduce plugging by forcing accumulated polymer chunks or particles through the valve. However, the duration and magnitude of the pressure pulse is not so large as to significantly affect the average pressure of the loop reactor. By moving the continuous take off valve at regular intervals, regardless of the detection of plugging, the operator can clear the continuous take off valve, ensure regular production of polymer and avoid plugging problems before they occur.

CLM What is claimed is:

> 6. A process for operating a loop polymerization reactor, the process comprising: feeding at least one olefin monomer and diluent to the reactor; feeding a polymerization catalyst to the reactor; circulating a fluid slurry comprising unreacted ethylene and solid polyethylene particles in the diluent through the reactor; continuously withdrawing a portion of the fluid slurry through a plurality of active continuous take off; and continuously flushing diluent through an inactive continuous take off.

CLM What is claimed is:

> 10. A process for starting a loop polymerization reactor, the process comprising: feeding ethylene to the reactor; and feeding isobutane to the reactor; wherein the mass ratio of ethylene to isobutane fed to the reactor is sufficiently low to avoid plugging of a continuous take off.

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L7 ANSWER 44 OF 53 USPAT2 on STN

ACCESSION NUMBER: 2004:101933 USPAT2
TITLE: Process for producing bimodal polyethylene resins

INVENTOR(S):

INVENTOR(S): Marechal, Philippe, Nivelles, BELGIUM
PATENT ASSIGNEE(S): Total Petrochemicals Research Feluy, Feluy, BELGIUM

(non-U.S. corporation)

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PATENT INFORMATION:	US 7034092	B2	20060425	
	WO 2002028922		20020411	
APPLICATION INFO.:	US 2001-398162		20011002	(10)
	WO 2001-EP11394		20011002	
			20031117	PCT 371 date

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PRIMARY EXAMINER: Lu, Caixia

LEGAL REPRESENTATIVE: Jackson, William D.

NUMBER OF CLAIMS: 22 EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 7 Drawing Figure(s); 6 Drawing Page(s)

LINE COUNT: 859

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

A process for producing bimodal polyethylene resins in two reactors in series, the process comprising producing a first polyethylene resin fraction in a first slurry loop reactor in a diluent in the presence of a catalyst and producing a second polyethylene resin fraction in a second slurry loop reactor, serially connected to the first reactor, in the diluent in the presence of the catalyst, the first polyethylene resin fraction being passed from the first reactor to the second reactor together with the catalyst, one of the first and second reactors producing a resin fraction of higher molecular than the resin fraction produced by the other of the first and second reactors, characterised in that the first reactor is fed with a feed of ethylene and diluent having an ethylene content of at least 70 wt % based on the weight of the diluent and in that in the first reactor the slurry of polyethylene in the diluent has a solids content of at least 30 wt % based on the weight of the diluent.

SUMM EP-A-649,860 discloses of process for co-polymerising ethylene in two liquid full loop reactors serially connected, wherein the comonomer is introduced in the first reactor, wherein the high molecular weight fraction of the polymer is produced in the first reactor and the low molecular weight fraction is produced in the second reactor and wherein the transfer from the first to the second reactor is operated through one or more settling legs.

SUMM EP-A-580,930 discloses a process for homo- or co-polymerising ethylene in two liquid full loop reactors serially connected, wherein the comonomer is introduced in the first reactor and wherein the concentration of hydrogen is very low in the first reactor and very high in the second reactor.

SUMM EP-A-832,905 discloses a process for preparing ethylene homoor co-polymers in two liquid full loop reactors serially connected, in the presence of a chromium-based catalyst, wherein a low molecular weight homopolymer of ethylene is produced in the first reactor and a high molecular weight homo- or co-polymer of ethylene is produced in the second reactor.

SUMM WO 92/12181 discloses a method for homo- or co-polymerising ethene in the presence of a Ziegler-Natta catalyst and a possible comonomer and hydrogen. The polymerisation is carried out in a loop reactors at a temperature higher than the critical temperature but lower than the melting temperature of ethene, and at a pressure higher than the critical pressure of the mixture.

In single slurry loop reactors for the production of monomodal polyethylene resins, it is known that if the pump which is provided in the loop reactor for circulating the slurry around the loop is provided with high output power, this can lead to higher solids concentration in the slurry circulating around the reactor. Furthermore, the solids concentration can also be increased by using a circulating pump having a diameter that is larger than the diameter of the reactor tube. This is achieved by providing a localised enlargement in the reactor tube at the location of the propeller or vanes of the pump. Furthermore,

it is known that the replacement of the conventional settling legs in a slurry loop reactor, which are provided for periodic and sequential take off of the polyethylene fluff by a so-called "continuous product take off" can also lead to higher solids concentration in the reactor.

- SUMM The present invention provides a process for producing bimodal polyethylene resins in two reactors in series, the process comprising producing a first polyethylene resin fraction in a first slurry loop reactor in a diluent in the presence of a catalyst and producing a second polyethylene resin fraction in a second slurry loop reactor, serially connected to the first reactor, in the diluent in the presence of the catalyst, the first polyethylene resin fraction being passed from the first reactor to the second reactor together with the catalyst, one of the first and second reactors producing a resin fraction of higher molecular than the resin fraction produced by the other of the first and second reactors, characterised in that the first reactor is fed with a feed of ethylene and diluent having an ethylene content of at least 70 wt % based on the weight of the diluent and in that in the first reactor the slurry of polyethylene in the diluent has a solids content of at least 30 wt % based on the weight of the diluent.
- DRWD FIG. 1 is a schematic diagram of an apparatus comprising two serially connected slurry loop reactors for use in an embodiment of the process for producing bimodal polyethylene resins in accordance with the present invention;
- DRWD FIG. 2 is an enlarged schematic view of part of a settling leg of the first slurry loop reactor of the apparatus of FIG. 1;
- DETD Referring to FIG. 1, there is shown schematically an apparatus for producing bimodal polyethylene resins in accordance with the invention in two reactors in series. The apparatus, designed generally as 2, comprises a first slurry loop reactor 4 and a second slurry loop reactor 6 serially connected thereto and downstream thereof. The first slurry loop reactor 4 is provided with a feed, indicated as feed No. 1, along an inlet line 8. Feed No. 1 comprises ethylene monomer, one of (a) a comonomer comprising at least one $\alpha-$ olefin having from 3 to 12 carbon atoms or (b) hydrogen, and a catalyst. The catalyst may comprise a Ziegler-Natta catalyst, a chromium-based catalyst, in particular comprising chromium oxide deposited on a support such as silica, a metallocene catalyst, or a LTM (Late Transition Metal) catalyst. The slurry loop reactor 4 is of generally known construction and is provided with a settling leg 10 which depends downwardly from the first slurry loop reactor 4. In this embodiment the settling leg 10 is located at the upper portion 9. At the bottom of the settling leg 10 is provided a valve 12 for selective and periodic removal of polyethylene fluff from the settling leg 10. In large scale reactors, there is a series of legs (like 10) and corresponding valves (like 12) operating successively. For continuous product take off, valve 12 remains open. An outlet line 14 communicates between the valve 12 and the second slurry loop reactor 6 for feeding from the first slurry loop reactor 4 to the second slurry loop reactor 6 the first polyethylene resin fraction produced in the first slurry loop reactor together with the catalyst. The first slurry loop reactor 4 is additionally provided with a pump 16 which includes a propeller 18 driven by a motor 20. The

- propeller 18 is located in a lower portion 22 of the first slurry loop reactor 4 and the lower portion 22 is provided with an increased internal diameter (D) compared to the internal diameter (d) of the remaining parts of the first slurry loop reactor 4.
- DETD The second slurry loop reactor 6 is also provided with a respective inlet line 24 through which a feed (feed No. 2) of additional ethylene monomer and one of (a) a comonomer comprising an α olefin having from 3 to 12 carbon atoms or (b) hydrogen are fed to the second slurry loop reactor 6. The second slurry loop reactor 6 is also provided with a respective settling leg 26 and associated valve 28, in this embodiment located at an upper portion 29 of the second slurry loop reactor 6. An outlet line 30 is provided at the downstream end of the valve 28 for feeding the ultimate bimodal polyethylene resin, comprising a blend of the first and second polyethylene resin fractions respectively produced in first and second reactors 4,6, for further processing, for example by an extruder (not shown).
- DETD The second slurry loop reactor 6 is additionally provided with a respective pump 32 comprising a propeller 34 driven by a motor 36.
- DETD In one aspect of the process of the invention, a relatively high molecular weight polyethylene resin fraction is produced in the first slurry loop reactor 4 by copolymerisation of ethylene and the comonomer and a relatively low molecular weight polyethylene resin fraction is produced in the second slurry loop reactor 6 by homopolymerisation of ethylene in the presence of hydrogen. In an alternative aspect of the invention the low molecular weight resin fraction is produced in the first slurry loop reactor 4 and the high molecular weight fraction is produced in the second slurry loop reactor 6. For either aspect, it has been found that the use of a high solids concentration in the first loop reactor leads to improved mechanical properties of the resultant bimodal polyethylene resin blend.
- DETD In accordance with the process of the invention, the slurry circulated around the first slurry loop reactor 4 by the pump 16 has a solids content of at least 30 wt % based on the weight of the diluent, more preferably from 30 to 60 wt % for a Ziegler-Natta catalyst or from 35 to 60 wt % for a metallocene catalyst. Most preferably, for either catalyst, the solids content of the slurry in the first slurry loop reactor 4 is at least 40 wt % or more preferably at least 45 wt % based on the weight of the diluent.
- DETD The higher solids content in the first loop reactor is achieved by providing that the feed for the first slurry loop reactor 4 has an ethylene content of at least 70 wt % based on the weight of the diluent, more preferably from 85 to 250 wt %, yet more preferably above 90 wt % for Ziegler-Natta catalysts and preferably from 90 to 250 wt %, more preferably above 110 wt %, based on the weight of the diluent, for a metallocene catalyst.
- DETD In the first slurry loop reactor 4, the first polyethylene resin fraction is polymerised and progressively the polyethylene resin fluff settles in the settling leg 10. An enlarged schematic view of the settling leg 10 is illustrated in FIG. 2. It may be seen that the polyethylene resin fluff 38 has progressively settled at the bottom of the settling leg 10. The valve 12 is ordinarily closed. When it is desired to transfer the first polyethylene resin fraction 38

from the first slurry loop reactor 4 to the second slurry loop reactor 6, together with the catalyst therein, the valve 12 is opened and a volume V, as shown in FIG. 2, of both the polyethylene resin fluff 38 and a minor proportion of slurry 40 is transferred along outlet line 14 to the second slurry loop reactor 6.

- DETD In order to enhance reactor independence between the first and second slurry loop reactors 4,6, it is desired that the proportion of slurry 40 in the volume V is minimized. This not only ensures a maximum efficiency in the transfer of the first polyethylene resin fraction 38 from the first reactor 4 to the second reactor 6, but also ensures that the transfer of comonomer or hydrogen, depending on, respectively, whether or not the high molecular weight or low molecular weight fraction is polymerised in the first slurry loop reactor 4, is transferred additionally in the volume V to the second slurry loop reactor 6. Desirably, the amount of comonomer or hydrogen transfer to the second slurry loop reactor is minimized in order to ensure reactor independence, leading not only to a high difference in density between the first and second polyethylene resin fractions, but also a large difference in the molecular weight. Ideally, the high molecular weight/low density polyethylene resin fraction should be as low as possible in density and high as possible in molecular weight. Equally, the low molecular weight/high density polyethylene resin fraction should be as high as possible in density and as low as possible in molecular weight.
- DETD Referring to FIG. 3, it may be seen that the amount of the polyethylene fluff in the region V shown in FIG. 2 tends to increase with an increase in the solids content of the slurry in the first slurry loop reactor. It may thus be seen that an increase of the solids content of the slurry circulated around the first slurry loop reactor enhances the proportion of polyethylene fluff transferred from the settling leg of the first reactor 4 to the second reactor 6, which in turn reduces the amount of comonomer or hydrogen transferred to the second reactor 6, which again in turn increases reactor independence. DETD Thus when using a Ziegler-Natta catalyst for example, the bulk density is relatively low and so the maximum solids content is achieved by utilising a maximum ethylene/diluent weight ratio in the first reactor of about 1.2. In contrast, when using a metallocene catalyst the maximum bulk density of the polyethylene fluff

is higher, up to about $0.5~\mathrm{g/cc}$, and this permits a higher maximum ethylene/diluent ratio of about $2.5~\mathrm{to}$ be employed. Around 92 to

99.5% of the ethylene feed into the first loop reactor is polymerised to polyethylene and so the ethylene/diluent ratio is selected for achieving the maximum solids content to achieve maximum settling, but with the corresponding minimum proportion of ethylene in the diluent which is dependent upon the achievable bulk density based on the catalyst employed.

The polymerisation temperature in the first loop

The polymerisation temperature in the first loop reactor 4 typically ranges from 70 to 100° C., most preferably about 80° C. when the HMW fraction is produced in the first reactor and from 80 to 120° C., most preferably around 95° C. when the LMW is produced in the first reactor. The polymerisation temperature also affects the particular solids content of the slurry employed, because an increase in temperature tends to lower the viscosity of the diluent. The polymerisation pressure is from 30 to 90 bars, most preferably about 41 bars.

DETD In order to use a higher solids content in the first slurry loop reactor 4, the minimum operating pump power of the pump 16 is relatively high and preferably the diameter D of the lower portion 22 of the first slurry loop reactor 4 in which the propeller 18 is located is increased to permit the pump more readily to circulate the higher solids content slurry around the first slurry loop reactor 4. The power needed to circulate a slurry having a given solids content around the reactor depends on the reactor diameter. If the reactor diameter is increased, less power is required, but that is at the expense of the cooling surface area and consequently at the expense of reactor throughput. For a reactor of particularly large size, the dissipation of such high power may require the provision of multiple pumping sections or a pumping section with a large pump diameter, which allows dissipation of the pumping power in a larger volume of slurry, thereby avoiding the potential of cavitation in the slurry. The provision of pumps in two different pumping sections has the drawback that there is a higher probability of bearing problems with two pumps and there is also a requirement for a long horizontal section between the two pumps or a reactor with a larger number of vertical legs. The present inventor has determined that for a variety of reactor sizes represented by a reactor volume, there is a preferred internal diameter for the reactor, a preferred pump minimum operating power and a most preferred pump minimum operating power. The corresponding values for three reactor sizes of 19,70 and 100 m.sup.3 are summarised in Table 1. DETD In the second slurry loop reactor 6, the inventor has found that the degree of settling of the polyethylene resin fluff in the settling leg 26 of the second slurry loop reactor 6 tends to increase with a corresponding increase in solid fraction and in the bulk density of the polyethylene resin fluff in the second slurry loop reactor 6. For large scale production of bimodal polyethylene pipe resins, the second slurry loop reactor 6 may additionally be provided with a larger diameter circulating pump 32 having a construction similar to that of the pump 16 for the first reactor 4 illustrated in FIG. 1 and continuous produce take-off through the settling leg 26, which would then be provided at the bottom of the loop. This would provide the advantages of high plant throughput and high catalyst productivity. The continuous product take off provides also the advantage of increasing plant reliability by eliminating a series of settling legs and corresponding valves. The present inventor has found that when the solids fraction of the slurry circulating around the first slurry loop reactor 4 is above 45 wt %, it is possible to employ, instead of periodic polyethylene fluff removal through the settling leg 10 illustrated in FIG. 1, continuous removal of the polyethylene fluff through a settling leg provided at the bottom of the reactor, which is thus absent a valve or which is just working with a open valve, this valve being closed for example for reactor filling operations. The polyethylene resin fraction produced in the first reactor is removed continuously from the settling leg and continuously transferred to the second reactor 6. DETD Provided the solids concentration is sufficiently high, that is above 45% of solids, this does not reduce significantly the reactor independence. Such continuous removal and transfer of the first polyethylene resin fraction tends to reduce the possibility of the settling leg being plugged by the resin and leakage problems. Moreover, it is believed by the inventor that the use of a continuous product

take-off as compared to a discontinuous produce take-off may tend to

increase the solids concentration in the first

slurry loop reactor 4.

- DETD The inventor has found that the use of a high solids concentration in the first loop reactor leads not only to improved mechanical properties of the polyethylene resin blend but also by maximising the solids concentration in the first reactor, in particular by using a larger pump diameter and optionally continuous product transfer of the polyethylene resin fraction to the second reactor at the end of a settling section, this leads to improved reactor throughput, improved product properties and improved catalyst productivity.
- DETD In accordance with one preferred aspect of the invention, the diluent may be present under supercritical conditions. Thus the diluent is at a pressure greater than the critical pressure Pc and at a temperature greater than the critical temperature Tc. Under these conditions, there is no thermodynamic transition between the gas phase and the liquid phase and the homogeneous supercritical fluid has the properties of a dense gas and a low density liquid. Either or both of the two loop reactors may be employed with supercritical diluent. When the first loop reactor is operated under supercritical conditions, the pressure is typically from 37 to 100 bars, more preferably from 50 to 90 bars, yet more preferably from 55 to 70 bars and the temperature is typically from 70 to 140° C., more preferably from 80 to 100° C. Under supercritical conditions, as a result of faster settling and increased packing of the polyethylene fluff at the bottom of the settling leg, significantly less diluent is additionally removed with the polyethylene resin fraction under supercritical conditions as compared to subcritical conditions. This assists in enhancing the independence of the two reactors.
- DETD The apparatus of FIG. 1 was employed to produce a bimodal polyethylene resin in which in the first slurry loop reactor a high molecular weight fraction was produced by copolymerisation of ethylene and 1-hexene and in the second slurry loop reactor the low molecular weight fraction was produced by homopolymerisation of ethylene in the presence of hydrogen. In the first reactor the temperature was 80 ° C. and the pressure was 42 bars and in the second reactor the temperature was 90° C. and the pressure was 41 bars. The catalyst comprised a Ziegler-Natta catalyst activated with an alkyl aluminium. The first reactor was fed with a feed of ethylene, comonomer and diluent, the diluent comprising isobutane, with the ethylene content of the feed being 71 wt % based on the weight of the diluent. The comonomer concentration in the first reactor was adapted to reach the required density, higher comonomer content resulting in lower density. The remaining process parameters, comprising the solids content in the first reactor (R1); the throughput through the reactors in tonnes per hour, the ratio of ethylene to diluent outputted from the first reactor (R1) (corresponding substantially (99%) to the ratio of ethylene to diluent inputted to the first reactor (R1)); the ratio between 1-hexene and ethylene in the second reactor (R2); and the ratio between the hydrogen and ethylene contents in the second reactor (R2), are specified in Table 2.
- CLM What is claimed is:
 - 1. A process for producing bimodal polyethylene resins in two reactors in series, the process comprising producing a first polyethylene resin fraction in a first slurry loop reactor in a diluent in the presence of a catalyst and producing a second polyethylene resin fraction in a second slurry loop reactor, serially connected to and downstream of the first reactor, in the diluent in the presence of the catalyst, the first polyethylene resin fraction being passed from the first reactor to the second reactor together with the

catalyst, producing in one of the first and second reactors a resin fraction of higher molecular weight than the molecular weight of the resin fraction produced by the other of the first and second reactors, supplying the first reactor with a feed of ethylene and diluent having an ethylene content of at least 70 wt. % based on the weight of the diluent wherein in the first reactor the slurry of polyethylene in the diluent has a solids content of at least 30 wt. % based on the weight of the diluent.

CLM What is claimed is:

14. A process for producing a bimodal polyethylene resin in first and second slurry loop reactors connected in a series comprising: (a) supplying a feed comprising a diluent, ethylene in an amount within the range of 70-250 wt. % based upon the weight of said diluent, an alpha olefin comonomer having from three to 12 carbon atoms and a polymerization catalyst to said first reactor; (b) copolymerizing said ethylene and said comonomer in said first reactor to produce a relatively high molecular weight copolymer resin fraction in said first reactor; (c) transferring said copolymer fraction, diluent and catalyst from said first slurry loop reactor to said second slurry loop reactor; (d) supplying a feed stream comprising ethylene and hydrogen to said second reactor; (e) polymerizing ethylene in the presence of hydrogen in said second reactor to produce a second polyethylene resin fraction in said second reactor by the homopolymerization of ethylene in the presence of hydrogen, said second polyethylene resin fraction having a lower molecular weight than the resin fraction produced in said first reactor; and (f) recovering a bimodal polyethylene resin comprising said copolymer and said homopolymer from said second reactor.

CLM What is claimed is:

21. A process for producing a bimodal polyethylene resin in first and second slurry loop reactors connected in a series comprising: (a) supplying a feed comprising a diluent, ethylene , hydrogen and a polymerization catalyst to said first reactor wherein the ethylene concentration in the feed supplied to said first reactor is within the range of 70-250 wt. % based upon the weight of the diluent; (b) polymerizing said ethylene in said first reactor to produce a relatively low molecular weight polyethylene resin fraction in a slurry in the diluent in said first reactor; (c) transferring said polyethylene resin fraction, diluent and catalyst from said first slurry loop reactor to said second slurry loop reactor; (d) supplying a feed stream comprising ethylene and a C.sub.3-C.sub.12 alpha olefin comonomer to said second reactor; (e) copolymerizing said ethylene and said C.sub.3-C.sub.12 alpha olefin comonomer in said second reactor to produce a second copolymer resin fraction in said second reactor by the copolymerization of ethylene and said C.sub.3-C.sub.12 alpha olefin, said second copolymer resin fraction having a higher molecular weight than the resin fraction produced in said first reactor; and (f) recovering a bimodal polyethylene resin comprising said copolymer and said homopolymer from said second reactor and supplying said bimodal polyethylene resin for further processing in an extruder without additional polymerization.

CLM What is claimed is:

22. A process for producing a bimodal polyethylene resin in first and second slurry loop reactors connected in a series comprising: (a) supplying a feed comprising a diluent, ethylene

, hydrogen and a metallocene polymerization catalyst to said first reactor; (b) polymerizing said ethylene in said first reactor to produce a relatively low molecular weight polyethylene resin fraction in a slurry in the diluent in said first reactor wherein said catalyst is a metallocene catalyst and the slurry in the first reactor has a solids content within the range of 35 to 60 wt. % based on the weight of the diluent; (c) transferring said polyethylene resin fraction, diluent and catalyst from said first slurry loop reactor to said second slurry loop reactor; (d) supplying a feed stream comprising ethylene and a C3-C12 alpha olefin comonomer to said second reactor; (e) copolymerizing said ethylene and said C3-C12 alpha olefin comonomer in said second reactor to produce a second copolymer resin fraction in said second reactor by the copolymerization of ethylene and said C3-C12 alpha olefin, said second copolymer resin fraction having a higher molecular weight than the resin fraction produced in said first reactor; and (f) recovering a bimodal polyethylene resin comprising said copolymer and said homopolymer from said second reactor and supplying said bimodal polyethylene resin for further processing in an extruder without additional polymerization.

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L7 ANSWER 45 OF 53 USPAT2 on STN

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TITLE: Slurry polymerization reactor

having large length/diameter ratio

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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Slurry polymerization reactor having large

length/diameter ratio

AB A polymerization loop reactor including a loop reaction zone, a continuous takeoff, and a fluid slurry disposed in the reaction zone. A generally cylindrical wall defines the loop reaction zone. The length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio greater than 250. The reactor can be charged with a fluid slurry including an olefin monomer reactant, solid olefin polymer particles, and a liquid diluent. The concentration of the solid olefin polymer particles in the slurry can be greater than 40 weight percent based on the weight of polymer particles and the weight of liquid diluent. Also disclosed is a polymerization process carried out by polymerizing, in the loop reaction zone of a reactor as defined above, at least one olefin

monomer in a liquid diluent to produce a fluid slurry as defined above.

SUMM Addition polymerizations are frequently carried out in a liquid that is

Addition polymerizations are frequently carried out in a liquid that is a solvent for the resulting polymer. When high-density (linear) ethylene polymers first became commercially available in the 1950's this was the method used. It was soon discovered that a more efficient way to produce such polymers was to carry out the polymerization under slurry conditions. More specifically, the polymerization technique of choice became continuous slurry polymerization in a pipe loop reactor with the product being taken off by settling legs that operated on a batch principle to recover product. This technique has enjoyed international success with billions of pounds of ethylene polymers being so produced annually. With this success

has come the desirability of building a smaller number of large reactors as opposed to a larger number of small reactors for a given plant capacity.

SUMM Settling legs, however, do present two problems. First, they represent the imposition of a "batch" technique onto a basic continuous process. Each time a settling leg reaches the stage where it "dumps" or "fires" accumulated polymer slurry it causes an interference with the flow of slurry in the loop reactor upstream and the recovery system downstream. Also the valve mechanism essential to periodically seal off the settling legs from the reactor upstream and the recovery system downstream requires frequent maintenance due to the difficulty in maintaining a tight seal with the large diameter valves needed for sealing the legs.

SUMM In spite of these limitations, settling legs have continued to be employed where olefin polymers are formed as a slurry in a liquid diluent. This is because, unlike bulk slurry polymerizations (i.e. where the monomer is the diluent) where solids concentrations of better than 60 percent are routinely obtained, olefin polymer slurries in a diluent are generally limited to no more than 37 to 40 weight percent solids. Hence settling legs have been believed to be necessary to give a final slurry product at the exit to the settling legs of greater than 37-40 percent. This is because, as the name implies, settling occurs in the legs to thus increase the solids concentration of the slurry finally recovered as product slurry.

SUMM Two pertinent patents addressing loop reactors for slurry polymerization are U.S. Pat. Nos. 6,239,235 and

6,204,344, each of which is incorporated here by reference in its entirety for its description of loop reactors and their diameters, lengths, equipment, and operation.

- One aspect of the invention is a charged polymerization loop reactor including a loop reaction zone, a continuous takeoff, and a fluid slurry disposed in the reaction zone. A generally cylindrical wall defines the loop reaction zone. The length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio greater than 250. The fluid slurry includes at least one olefin monomer reactant, solid olefin polymer particles, and a liquid diluent. The concentration of the solid olefin polymer particles in the slurry is greater than 40 weight percent based on the weight of polymer particles and the weight of liquid diluent. The continuous take off is provided for continuously withdrawing the fluid slurry from the loop reaction zone.
- SUMM Another aspect of the invention is a polymerization loop reactor including a loop reaction zone and a continuous takeoff. A generally cylindrical wall defines the loop reaction zone. The length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio greater than 1000. The continuous take off is provided for continuously withdrawing a fluid slurry from the loop reaction zone.
- DRWD FIG. 1 is a schematic perspective view of a loop reactor and polymer recovery system;
- DRWD FIG. 5 is a side view of an elbow of the loop reactor showing both a settling leg and continuous take off assemblies;
- DETD Surprisingly, it has been found that continuous take off of product slurry in an olefin polymerization reaction carried out in a loop reactor in the presence of an inert diluent allows operation of the reactor at a much higher solids concentration. Commercial production of predominantly ethylene polymers in isobutane diluent has generally been limited to a maximum solids concentration in the reactor of 37-40 weight percent. However, the continuous take off has been found to allow significant increases in solids concentration. Furthermore, the continuous take off itself brings about some additional increase in solids content as compared with the content in the reactor from which it takes off product because of the placement of the continuous take off appendage, which selectively removes a slurry from a stratum where the solids are more concentrated. Hence concentrations of greater than 40 weight percent are possible in accordance with this invention.
- DETD The present invention is applicable to any olefin polymerization in a loop reactor utilizing a diluent so as to produce a product slurry of polymer and diluent. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The invention is particularly suitable for the homopolymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.01 to 10, preferably 0.01 to 5, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient

- comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer.
- DETD Referring now to the drawings, there is shown in FIG. 1 a loop reactor 10 having vertical segments 12, upper horizontal segments 14 and lower horizontal segments 16 of reactor piping, some or all of which have generally cylindrical walls, joined end to end by junctions such as elbows to form a complete circuit or loop, sometimes referred to as a loop reaction zone, of a certain length. These upper and lower horizontal segments define upper and lower zones of horizontal flow. In this embodiment, each bend or elbow 20 is smooth, thus providing a continuous flow path substantially free from internal obstructions.
- DETD The reaction slurry is circulated by an impeller 22 (shown in FIG. 8) driven by a motor 24. As shown in FIG. 8, the impeller 22 and the casing or reactor wall surrounding the impeller can be greater in diameter than the general diameter of the piping forming the reactor. This feature is particularly desirable where the loop reactor has a high length/outside diameter ratio, creating greater resistance to flow around the loop than would be found in a loop having a lower ratio.
- DETD Since the volumetric flow of material is essentially identical through each cross-section of the reactor, the use of a larger-diameter impeller 22 and a larger impeller motor 24 than usual for the general size of pipe in the loop increases the velocity of flow through the normal-diameter piping. An increased velocity is desirable to avoid the need for additional time for the components of the slurry to travel around the loop in a reactor having a high Length/Outside Diameter ratio.
- DETD It will also be appreciated that the reactor loop may have more than one impeller or more than one impeller/motor combination in series around the loop. The series impellers may be close together, distributed about the loop, or otherwise arranged in any appropriate manner. It is contemplated that existing pump technology can support a reactor of roughly 44,000 or 45,000 gallons (166 or 170 m.sup.3), depending on its diameter and configuration. This assumes a circulation velocity of 32 ft/s (9.75 m/s) is maintained.
- Referring to the Figures, the reacting monomer, comonomer, if any, and make up diluent are introduced via lines 26 and 28 respectively which can enter the reactor directly at one or a plurality of locations or can combine with the condensed diluent recycle line 30 as shown. The catalyst is introduced via a catalyst introduction port 32, which provides a zone (location) for catalyst introduction. The elongated hollow appendage for continuously taking off an intermediate product slurry is designated broadly by the reference character 34. The continuous take off mechanism 34 is located in or adjacent to a downstream end of one of the lower horizontal reactor loop sections 16 and adjacent or on a connecting elbow 20. While continuous take off is generally preferred, the reactor could also be used with settling legs or intermittent take off, in whole or in part, without departing from certain aspects of the invention.
- DETD The continuous take off appendage is shown at the downstream end of a lower horizontal segment of the loop reactor, which is the preferred location. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. However, the continuous take off appendage can be located on any segment or any elbow.
- DETD As can be seen from the relative sizes, the continuous take off cylinders are much smaller than the conventional settling legs. Yet three 2-inch (5-cm) ID continuous take off appendages can remove as much

product slurry as fourteen 8-inch (20-cm) ID settling legs. This is significant because with current large commercial loop reactors of 15,000-18,000 gallon (57-68 m.sup.3) capacity, six 8-inch (20-cm) settling legs are required. It is not desirable to increase the size of the settling legs because of the difficulty of making reliable valves for larger diameters. As noted previously, doubling the diameter of the pipe increases the volume four-fold and there simply is not enough room for four times as many settling legs to be easily positioned. Hence, the invention makes feasible the operation of larger, more efficient reactors. Reactors of 30,000 gallons (114 m.sup.3) or greater are made possible by this invention. Generally the continuous take off cylinders will have a nominal internal diameter within the range of 1 inch (2.5 cm) to less than 8 inches (20 cm). Preferably they will be about 2-3 inches (5-7.5 cm) internal diameter. Commercial pumps for utilities such as circulating the reactants in a closed loop reactor are routinely tested by their

DETD manufacturers and the necessary pressures to avoid cavitation are easily and routinely determined.

DETD Representative loop reactor length/reactor outside diameter ratios are calculated in Table 5 for the various loop reactors described in U.S. Pat. Nos. 6,239,235 and 6,204,344. In Table 5, the "Row" column is added for easy reference to a particular row of data. The "Reference" column indicates which patent discloses the reactor in question (the '235 patent or the '344 patent), and at what column and line of the patent the disclosure is found. (for example, the first entry indicates a description in the '235 patent, col. 7, lines 12-14). "OD" indicates the nominal or outside diameter of the reactor pipe (this should not be confused with the diameter of the loop, which would be much greater), "ID" indicates the inside diameter of the reactor pipe. "Length" is the length of the reactor (i.e. one circuit of the reactor loop). "Vol." is the volume of the reactor. "L/OD ratio" is the ratio of the reactor length to the pipe diameter, expressed in the same units so the

ratio is unitless. Speaking more generally, the inventors contemplate that the Length/Outside Diameter ratio of a loop reactor

DETD should be increased to a greater value than the corresponding ratios of preexisting reactors, to provide a more favorable ratio of reactor volume to heat transfer area, for more efficient cooling. If the ratio is increased by using relatively small diameter piping for the loop, a double advantage to heat transfer is gained. First, the area of the piping in relation to its volume increases. Second, the wall thickness of the piping can be reduced, as smaller-diameter piping is stronger per unit surface area and the saltation velocity of the slurry is lower, so the pressure head can be reduced. Both factors increase heat transfer across the pipe wall.

DETD TABLE 4

(English Units)

Description	24 in Pump	26 in Pump	26 in Pump + CTO
Avg. Reactor Solids Concentration, wt. %		53	
Polymer Production Rate, mlbs/hr	40.1	40.7	39.9
Reactor Circulation Pump Power, kw	430	691	753
Circulation Pump	14.3	22.4	23.7

D C			
Pressure Diff, psi Circulation Pump	61.8	92.5	92.4
Head, ft	01.0	92.5	92.4
Reactor Slurry Flow	39	46	45
Rate, mGPM			
Reactor Slurry	0.534	0.558	0.592
Density,			
gm/cc Reactor Temperature,	215.6	218.3	217.0
F.	213.0	210.5	217.0
Ethylene	4.43	3.67	4.9
Concentration,			
wt %			
Hexene-1	0.22	0.17	0.14
Concentration, wt %			
Reactor Heat	270	262	241
Transfer	_	202	
Coefficient			
Reactor Inside	22.0625	22.0625	22.0625
Diameter, inches	10700	10700	10700
Reactor Volume, gal Reactor Length, ft	18700 941	18700 941	18700 941
Pressure Drop per	0.066	0.098	0.098
Foot of Reactor, ft/ft		0 7 0 3 0	
(Metric Units)			
Danasiskias	0 C1 m D	0 CC m D	0.66 m Pump +
Description	0.61 m Pump	0.66 m Pump	CTO
Avg. Reactor Solids	39	45	53
concentration, wt. %			
Polymer Production	18.2	18.5	18.1
Rate, metric tons/hr	400	604	
Reactor Circulation Pump Power, kw	430	691	753
Circulation Pump	9.86	15.4	16.3
Pressure Diff, N/cm.su		10.1	10.0
Circulation Pump	18.8	28.2	28.2
Head, m			
Reactor Slurry Flow	148	174	170
Rate, m.sup.3/min Reactor Slurry	0.534	0.558	0.592
Density,	0.554	0.550	0.392
gm/cc			
Reactor Temperature,	102.0	103.5	102.7
EC		0.65	
Ethylene	4.43	3.67	4.9
Concentration, wt %			
Hexene-1	0.22	0.17	0.14
Concentration,			
wt %			
Reactor Heat			
Transfer Coefficient			
Reactor Inside	56.04	56.04	56.04
Diameter, cm	= 3 • • =		
Reactor Volume, m.sup.		70.80	70.80
Reactor Length, m	287	287	287

Pressure Drop per 0.066 0.098 0.098
Meter of Reactor,
m/m

"CTO" means "Continuous Take Off" CLM What is claimed is:

1. A polymerization loop reactor comprising: a loop reaction zone configured to polymerize an olefin monomer into a polyolefin in the presence of a diluent and defined by a generally cylindrical wall having a nominal outside diameter of at least 22 inches (55 cm), wherein a length/diameter (L/D) ratio of the generally cylindrical wall is in the range of 700 to about 1500; an impeller disposed within the loop reaction zone within a casing portion of the generally cylindrical wall, the casing portion having a first inside diameter, and the remaining portion of the cylindrical wall having at least a second inside diameter, wherein the first inside diameter is larger than the second inside diameter; and a continuous take off (CTO) positioned along the generally cylindrical wall and configured to substantially continuously withdraw a discharge slurry having a solids concentration greater than an average solids concentration of the slurry circulating through the loop reaction zone.

- CLM What is claimed is:
 2. The polymerization loop reactor of claim 1, wherein the solids concentration of the discharge slurry is greater than 50 weight percent.
- CLM What is claimed is:
 3. The polymerization loop reactor of claim 1,
 wherein a flow path of the CTO is configured substantially tangential to
 a curvature of an elbow of the generally cylindrical wall.
- CLM What is claimed is:
 4. The polymerization loop reactor of claim 1,
 wherein a diameter of the impeller is at least as large as the second inside diameter of the generally cylindrical wall.
- CLM What is claimed is:
 5. The polymerization loop reactor of claim 1,
 wherein the casing portion of the generally cylindrical wall has a first
 nominal outside diameter and the remaining portion of the generally
 cylindrical wall has at least a second nominal outside diameter, wherein
 the first nominal outside diameter is larger than the second nominal
 outside diameter.
- CLM What is claimed is:
 6. The polymerization loop reactor of claim 5,
 wherein the first nominal outside diameter is at least about 2 inches larger than the second nominal outside diameter.
- CLM What is claimed is:
 7. The polymerization loop reactor of claim 6,
 wherein the impeller is sized to circulate at least about 34,000 gallons
 per minute (gpm) of the slurry through the loop reaction zone.
- CLM What is claimed is:

 8. The polymerization loop reactor of claim 1,
 wherein the nominal outside diameter is about 24 inches (57 cm), about
 26 inches (66 cm), about 28 inches (70 cm), or about 30 inches (76 cm).

- CLM What is claimed is:

 9. The polymerization loop reactor of claim 1,
 wherein a size and a geometry of the impeller are configured to provide
 for circulation of the slurry through the loop reaction zone at a
 velocity greater than the saltation velocity of the slurry.
- CLM What is claimed is:
 10. The polymerization loop reactor of claim 1,
 wherein the loop reactor zone has a volume of at
 least 22,000 gallons (84 m.sup.3).
- CLM What is claimed is:
 11. The polymerization loop reactor of claim 1,
 wherein the loop reactor zone has a volume of at
 least 40,000 gallons (152 m.sup.3).
- CLM What is claimed is:
 12. The polymerization loop reactor of claim 1,
 wherein the loop reactor zone has a volume at least
 45.000 gallons (76 m.sup.3).
- CLM What is claimed is:
 13. The polymerization loop reactor of claim 1,
 wherein the loop reactor zone has a volume of
 greater than 30,000 gallons (114 m.sup.3).
- CLM What is claimed is:
 14. The polymerization loop reactor of claim 1,
 wherein an average solids concentration of the
 slurry circulating through the loop reaction zone is greater than about
 50 weight percent.
- CLM What is claimed is:
 15. The polymerization loop reactor of claim 1,
 wherein the CTO is configured to facilitate pressure control of the loop
 reaction zone.
- CLM What is claimed is: 16. A polymerization loop reactor comprising: a loop sluny reactor configured to polymerize olefin into polyolefin, and comprising: a reaction zone having a volume of at least about 22,000 gallons and defined by a generally cylindrical wall having a nominal outside diameter of at least 22 inches (55 cm), wherein a ratio of a length of the loop reaction zone to the nominal outside diameter is in the range of 700 to about 1500; an in-line impeller disposed in the reaction zone, wherein a first inside diameter of a casing portion of the generally cylindrical wall surrounding the in-line impeller is larger than a second inside diameter of a remaining portion of the generally cylindrical wall, wherein the in-line impeller and associated motor are configured to circulate a polyolefin slurry through the loop reaction zone at a velocity greater than a saltation velocity of the slurry; and a continuous take off (CTO) configured to substantially continuously withdraw the slurry from the loop reaction zone and to facilitate pressure control of the loop reaction zone.
- CLM What is claimed is:
 18. A polymerization loop reactor comprising: a
 loop reaction zone configured to polymerize olefin

into a polyolefin, and defined by a generally cylindrical wall having a nominal outside diameter of at least 22 inches, wherein the length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio in the range of 700 to about 1500; an in-line axial pump comprising an external motor, a casing, and an in-line impeller disposed within the casing, the casing having a casing nominal outside diameter at least about 2 inches larger than the nominal outside diameter of the generally cylindrical wall; and a plurality of continuous take offs configured to continuously withdraw a fluid slurry from the loop reaction zone.

CLM What is claimed is:

19. The polymerization loop reactor of claim 18, wherein a diameter of the impeller is at least as large as an inside diameter of the generally cylindrical wall.

CLM What is claimed is:

20. A polyethylene production system comprising: a loop slurry reactor comprising: a loop reaction zone configured to polymerize ethylene into polyethylene and defined by a generally cylindrical wall having a nominal outside diameter of at least 22 inches, wherein the length of the loop reaction zone and the nominal outside diameter of the generally cylindrical wall define a length/diameter ratio in the range of 700 to about 1500; an impeller configured to circulate a slurry through the loop reaction zone at a velocity greater than a saltation velocity of the slurry, wherein the slurry comprises polyethylene solid particles in a liquid diluent, and the velocity is at least 32 feet per second; and a continuous take off (CTO) configured to substantially continuously withdraw a discharge slurry from the loop reaction zone and to facilitate pressure control of the loop reaction zone, wherein the CTO is positioned along the generally cylindrical wall to so that the discharge slurry has a solids concentration higher than an average solids concentration of the circulating slurry; and a flash chamber configured to receive the discharge slurry and to vaporize liquid diluent in the discharge slurry.

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L7 ANSWER 53 OF 53 USPAT2 on STN

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TITLE: Continuous slurry polymerization

volatile removal

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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Continuous slurry polymerization volatile removal

AΒ A process/apparatus is disclosed for continuously separating a liquid medium comprising diluent and unreacted monomers from a polymerization effluent of a slurry loop reactor containing a flow of slurry therein, comprising a discharge conduit extending a distance into the loop reactor; the conduit having a longitudinal axis and an opening inside the loop reactor; at least a portion of the conduit being curved along its longitudinal axis inside the loop reactor; and the opening substantially facing the flow of the slurry, wherein the discharge conduit is located within a lower leg of the loop reactor such that a continuous discharge of the polymerization effluent from a slurry reactor through a discharge valve and transfer conduit into a first intermediate pressure flash tank wherein volatile inert diluent and unreacted monomers are removed and the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom to a second flash tank at a lower pressure.

SUMM The present invention relates to an apparatus for continuously separating polymer solids from a liquid medium comprising an inert diluent and unreacted monomers in a slurry polymerization process. In particular, the present invention relates to an apparatus for continuously separating polymer solids from a liquid medium, drying the polymer, and recovering the diluent and unreacted monomers with a reduction in compression needed for diluent vapor condensation to liquid diluent for reuse in the polymerization process. In another aspect, the invention relates to a method for continuously separating polymer solids from a liquid medium. In particular, the invention relates to a method for continuously separating polymer solids from a liquid medium, drying the polymer, and recovering the inert diluent and unreacted monomers for reuse in the polymerization process.

In many polymerization processes for the production of polymer, a polymerization effluent is formed which is a slurry of particulate polymer solids suspended in a liquid medium, ordinarily the reaction diluent and unreacted monomers. A typical example of such processes is disclosed in Hogan and Bank's U.S. Pat. No. 2,285,721, the disclosure of which is incorporated herein by reference. While the polymerization processes described in the Hogan document employs a catalyst comprising chromium oxide and a support, the present invention is applicable to any process producing an effluent comprising a slurry of particulate polymer solids suspended in a liquid medium comprising a diluent and unreacted

monomer. Such reaction processes include those which have come to be known in the art as particle form polymerizations.

SUMM In most commercial scale operations, it is desirable to separate the polymer and the liquid medium comprising an inert diluent and unreacted monomers in such a manner that the liquid medium is not exposed to contamination so that the liquid medium can be recycled to the polymerization zone with minimal if any purification. A particularly favored technique that has been used heretofore is that disclosed in the Scoggin et al, U.S. Pat. No. 3,152,872, more particularly the embodiment illustrated in conjunction with FIG. 2 of that patent. In such processes the reaction diluent, dissolved monomers, and catalyst are circulated in a loop reactor wherein the pressure of the polymerization reaction is about 100 to 700 psia. The produced solid polymer is also circulated in the reactor. A slurry of polymer and the liquid medium is collected in one or more settling legs of the slurry loop reactor from which the slurry is periodically discharged to a flash chamber wherein the mixture is flashed to a low pressure such as about 20 psia. While the flashing results in substantially complete removal of the liquid medium from the polymer, it is necessary to recompress the vaporized polymerization diluent (i.e., isobutane) in order to condense the recovered diluent to a liquid form suitable for recycling as liquid diluent to the polymerization zone. The cost of compression equipment and the utilities required for its operation often amounts to a significant portion of the expense involved in producing polymer.

SUMM In accordance with the present invention, there is provided an apparatus for continuously recovering polymer solids from a polymerization effluent comprising a slurry of the polymer solids in a liquid medium comprising an inert diluent and unreacted monomers. The apparatus comprises a discharge valve on a slurry reactor, examples of which include slurry loop reactors and stirred tank slurry reactors, for the continuous discharge of a portion of the slurry reactor contents into a first transfer conduit: a first flash tank having a bottom defined by substantially straight sides inclined at an angle to the horizontal equal to or greater than the angle of slide of the slurry/polymer solids; wherein the pressure of the first flash tank and temperature of the polymerization effluent are such that from about 50% to about 100% of the liquid medium will be vaporized and the inert diluent component of the vapor is condensable, without compression, by heat exchange with a fluid having a temperature in the range of about 65° F. to about 135° F.: a first flash tank exit seal chamber, communicating with the first flash tank, of such a length (1) and diameter (d) as to permit such a level of concentrated polymer solids/slurry to accumulate and form a pressure seal in the first flash tank exit seal chamber: a seal chamber exit reducer providing for a continuous discharge of a plug flow of concentrated polymer solids/slurry to a second transfer conduit which communicates the concentrated polymer solids/slurry into a second flash tank wherein the pressure of the second flash tank and temperature of the concentrated polymer solids/slurry are such that essentially all of any remaining inert diluent and/or unreacted monomer will be vaporized and removed overhead for condensation by compression and heat exchange and the polymer solids are discharged from the bottom of the second flash tank for additional processing or storage.

SUMM The invention provides also a method for the continuous removal of a

stream of polymerization effluent from a slurry reactor through a discharge valve; increasing the heat content of the polymerization effluent during its transit through the first transfer conduit to a temperature below the fusion point of the polymer while continuously communicating the polymerization effluent to a first flash tank having a bottom defined by substantially straight sides inclined at an angle to the horizontal equal to or greater than the angle of slide of the concentrated polymer solids/slurry; continuously vaporizing from about 50% to about 100% of the liquid medium in the first heated flash tank to yield a concentrated polymer solids/slurry and a vapor stream at such a temperature and pressure that the inert diluent content of the vapor is condensable, without compression, by heat exchange with a fluid having a temperature in the range from about 65° F. to about 135° F.; continuously discharging the concentrated polymer solids/slurry from the first flash tank to a first flash tank exit seal chamber of such a length (1) and diameter (d) that a volume of concentrated polymer solids/slurry is continuously maintained so as to form a pressure seal in the first flash tank exit seal chamber; continuously discharging the concentrated polymer solids/slurry from the first flash tank seal chamber through a seal chamber exit reducer defined by substantially straight sides inclined at an angle to that of horizontal equal to or greater than the angle of slide of the polymer solids which remain after removal of about 50 to 100% of the inert diluent therefrom; communicating a continuous plug flow of concentrated polymer solids/slurry from the first flash tank exit seal chamber through the seal chamber exit reducer to a second transfer conduit which communicates the continuous plug flow of concentrated polymer solids/slurry to a second flash tank; and continuously vaporizing essentially all of any remaining inert diluent and/or unreacted monomer in a second flash tank operated at a lower pressure than the first flash tank; condensing the vaporized inert diluent and/or unreacted monomer from the second flash tank by compression and heat exchange; and continuously discharging the essentially dried polymer slurry from the second flash tank for further processing or storage.

SUMM The present invention also relates to an apparatus for capturing a higher weight percentage of polymer solids from a circulating slurry in a loop reactor than the weight percentage of solids in the circulating slurry. The apparatus includes a conduit having a first end, wherein the first end extends for a distance into the loop reactor. The conduit also has portions defining an opening wherein the opening is positioned relative to the direction of the circulating slurry. Desirably, the opening may be facing the direction of flow of the circulating slurry. Additionally, a portion of the conduit may extend outwardly from the loop reactor for discharging, continuously or otherwise the polymer solids from the loop reactor.

The present invention also provides a process for capturing a higher weight percentage of polymer solids from a circulating slurry in a loop reactor than the weight percentage of polymer solids in the circulating slurry. This process includes the step of extending for a distance into a the loop reactor a conduit having portions defining an opening wherein the opening is extends into the circulating slurry. Additionally, this process may include the step of discharging, continuous or otherwise, the polymer solids from the loop reactor through a portion of the conduit extending outwardly from the loop reactor

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SUMM The present invention also provides a slurry loop reactor containing a flow of slurry therein which comprises a discharge conduit extending a distance into the loop reactor, the conduit having a longitudinal axis and an opening inside the loop reactor and at least a portion of the conduit being curved along its longitudinal axis inside the loop reactor, and the opening substantially facing the flow of the slurry. In one embodiment, the discharge conduit is located within a curved portion of the loop reactor. In another embodiment, the curved portion of the loop reactor comprises a lower leg of the loop reactor. Preferably, the discharge conduit is located within a middle portion of the curved portion of the loop reactor. Even more preferably, the discharge conduit is located substantially at the middle of the curved portion of the loop reactor. In another preferred embodiment in accordance with the present invention, the curved portion comprises a 20 to 270 degree bend, preferably a 80 to 200 degree bend, more preferably a 90 to 180 degree bend, and most preferably a 180 degree bend.

In another embodiment, the opening of the discharge conduit is located SUMM inside the loop reactor at a point where the concentration of solids of the slurry is higher than the average concentration of solids in the slurry in the loop reactor. Preferably, the opening is located closer to the outside wall of the loop reactor than to the inside wall of the loop reactor. More preferably, the opening is located closer to an outside wall of the loop reactor than to the center of the loop reactor. Even more preferably, the opening is closely adjacent to the outside wall of the loop reactor. Most preferably, the opening touches the outside wall of the loop reactor. In yet another preferred embodiment, the discharge conduit is curved along its longitudinal axis from about 45 degrees to about 135 degrees, preferably from about 75 degrees to about 135 degrees. In another embodiment, the face of the opening defines a plane which intersects an outside wall of the loop reactor at a tangent line which is substantially perpendicular to the plane. In yet another embodiment, the discharge conduit has a diameter which is about 5-40% of the inside diameter of the loop reactor , preferably about 7-25%, and more preferably about 8-15%.

SUMM The present invention also provides an apparatus for purging polymer solids from a conduit connected to a loop reactor and in fluid communication with the loop reactor. This apparatus includes a sensor, a first valve in fluid communication with the conduit, a second valve positioned between a first inert diluent and the conduit, wherein the first inert diluent is in fluid communication with the conduit between the loop reactor and the first valve. In response to a signal produced by the sensor, the first valve is closed and the second valve is opened allowing the first inert diluent to enter the conduit in sufficient quantities and under sufficient pressure to purge polymer solids from the conduit. This apparatus may further include a third valve positioned between a second inert diluent and the conduit, wherein the second inert diluent is in fluid communication with the conduit between the loop reactor and the first valve. In this way, when the first valve is open and the second valve is closed the third valve is opened allowing the second inert diluent to enter the conduit.

- SUMM The present invention also provides a process for purging polymer solids from a conduit connected to a loop reactor and in fluid communication with the loop reactor comprising. This process includes the steps of (i) closing a first valve in response to a first signal from a first sensor, wherein the first valve is connected to and in fluid communication with the conduit, (2) opening a second valve in response to a second signal from a second sensor, wherein the second valve is fluid communication between a first inert diluent and the conduit, and wherein the first inert diluent is in fluid communication with the conduit between the loop reactor and the first valve, and (3) flowing sufficient quantities of the first inert diluent under sufficient pressure into the conduit to purge polymer solids from the conduit. In this process the first and second sensors may be a common sensor and the first and second signal may be a common signal.
- SUMM The present invention also provides an apparatus for returning fines to a polymerization slurry in a loop reactor. The apparatus includes a discharge valve for discharging a portion of the polymerization slurry from the loop reactor into a first transfer conduit. The first transfer conduit communicates the polymerization slurry into a first flash tank. The first flash tank converts a portion of the polymerization slurry into a first fluid, such as a vapor. The first fluid includes a portion of the diluent and the fines from the polymerization slurry . A second transfer conduit communicates the first fluid to a first cyclone. The first cyclone converts a portion of the first fluid into a second fluid, such as a vapor. The second fluid includes a portion of the diluent and the fines. A third transfer conduit communicates the second fluid into a heat exchanger. The heat exchanger converts the second fluid into a liquid comprising the diluent and the fines. A fourth transfer conduit returns the liquid to the polymerization slurry in the loop reactor. This apparatus may also include a first transfer conduit heater for heat exchange between the first transfer conduit heater and the polymerization slurry.
- The present invention also provides a process for returning fines to a SUMM polymerization slurry in a loop reactor. The process includes (i) discharging a portion of the polymerization slurry from the loop reactor, (ii) communicating the discharge polymerization slurry into a first flash tank, (iii) converting in the flash tank a portion of the polymerization slurry into a first fluid, the first fluid comprising a diluent and the fines, (iv) communicating the first fluid from the first flash tank to a first cyclone, (v) converting in the cyclone a portion of the first fluid into a second fluid comprising the diluent and the fines, (vi) communicating the second fluid into a heat exchanger, (vii) converting in the heat exchanger the second fluid into a liquid comprising the diluent and the fines, and (viii) returning the liquid to the polymerization slurry in the loop reactor.
- SUMM The present invention further provides an apparatus and process for producing polymer from a polymerization slurry in a loop reactor operating at a space time yield greater than 2.8 lbs/hr-gal. In this instance, the polymer is formed in the polymerization slurry which includes a liquid medium and solids. The polymerization slurry is discharged

into a first transfer conduit. The polymerization slurry is referred to as a polymerization effluent upon leaving the loop reactor. The polymerization effluent is heated in the first transfer conduit to a temperature below the fusion temperature of the polymer solids. The heated polymerization effluent is communicated through the first transfer conduit to a first flash tank. In the first flash tank, from about 50% to about 100% of the liquid medium is vaporized. The vapor is condensed by heat exchange. Polymer solids are discharge from the first flash tank to a second flash tank through a seal chamber of sufficient dimension such as to maintain a volume of polymer solids in the seal chamber sufficient to maintain a pressure seal. The polymer solids are then communicated to a second flash tank. In the second flash tank, the polymer solids are exposed to a pressure reduction from a higher pressure in the first flash tank to a lower pressure in the second flash. The polymer solids are then discharging from the second flash tank. Additionally, the weight percent of solids in the polymerization slurry may be greater than 47. The loop reactor may be operated at a total recirculating pumping head/reactor distance of greater than 0.15 ft/ft. The loop reactor may also be operated with a recirculating pumping head greater than or equal to 200 ft. and have more than eight vertical legs, desirably between 10 and 16 vertical legs, more desirably between 10 and 12 vertical legs, most desirably 12 vertical legs. The volume of polymerization slurry in the loop reactor may be greater than 20,000 gallon.

- Another object of the present invention is to increase the reactor throughput by the use of continuous discharge and increased ethylene concentrations in the liquid medium, e.g., greater than or equal to 4 weight percent at reactor outlet, desirably from 4 weight percent to 8 weight percent, still more desirably from 5 weight percent to 7 weight percent.

 Settling legs limit ethylene concentrations due to an increased tendency to plug downstream equipment caused by accelerated reaction within the settling leg. A continuous polymerization effluent slurry flow allows ethylene concentrations to be limited only by the ethylene solubility in the liquid diluent in the reactor, thereby increasing the specific reaction rate for polymerization and increasing reactor throughput.
- SUMM Another object of the present invention is to increase the weight percent (wt %) of polymer solids in the polymerization slurry circulating in the polymerization zone in the loop reactor. Desirably, the wt % of polymer solids in the polymerization slurry is greater than 45, more desirably, from 45 to 65, still more desirably from 50 to 65, and most desirably from 55 to 65.
- The claimed apparatus and process provide several advantages over the prior art including: (1) allowing for a continuous processing of the contents of a slurry reactor from the point of discharge of the polymerization slurry effluent through a discharge valve; a first flash tank; a seal chamber; a seal chamber exit reducer; and therefrom to a second flash tank, (2) significantly increasing ethylene concentration in the loop reactor liquid medium thereby increasing reactor through-put, (3) significantly increasing the wt % of polymer solids in the polymerization slurry, (4) significantly increasing

- reactor space time yield and (5) energy consumption is reduced by reducing the need to compress and/or distill the reactor vapor-liquid effluent. Recycling compressors and other downstream equipment can be reduced in size or eliminated.
- DRWD FIG. 3 is an enlarged, cross sectional view of the discharge conduit with opening extending a distance into the loop reactor and the circulating polymerization slurry.
- DRWD FIG. 5 is an enlarged, cross sectional view of the curved discharge conduit with opening extending a distance into the loop reactor and the circulating polymerization slurry.
- DRWD FIG. 6 is a schematic view of a loop reactor having top and bottom legs having a generally 180 degree bend and a discharge conduit located in a bottom portion of a bend.
- DRWD FIG. 7 is a transverse cross sectional view of a bottom section of loop reactor taken generally along line 7--7 of FIG.
- DETD As used herein, the term "polymerization slurry"

 means substantially a two phase composition including polymer solids and liquid circulating within the loop reactor. The solids include catalyst and a polymerized olefin, such as polyethylene. The liquids include an inert diluent, such as isobutane, with dissolved monomer, comonomer, molecular weight control agents, such as hydrogen, antistatic agents, antifouling agents, scavengers, and other process additives.
- DETD As used herein, the term "space time yield" (STY) means the production rate of polymer per unit of loop reactor volume or polymerization slurry volume.
- DETD As used herein, the term "catalyst productivity" means weight of polymer produced per weight of catalyst introduced into the loop reactor.
- DETD As used herein, the term "polymer residence time" means the average duration that a polymer particle remains within the loop reactor.
- DETD The present invention is applicable to any mixture which comprises a slurry of polymer solids and a liquid medium comprising an inert diluent and unreacted polymerizable monomers including slurries resulting from olefin polymerization. The olefin monomers generally employed in such reactions desirably include 1-olefins having from 2 up to 8 carbon atoms per molecule. Typical examples include ethylene, propylene, butene, pentene, hexene and octene. Other examples include vinyl aromatic monomers, like styrene and alkyl-substituted styrene, geminally distributed monomers such as isobutylene and cyclic olefins, such as norbornene and vinyl norbornene. Typical diluents employed in such olefin polymerizations include saturated aliphatic hydrocarbons having 3 to 8, preferably 3 to 4 carbon atoms per molecule, such as propane, isobutane, propylene, n-butane, n-pentane, isopentane, n-hexane, isooctane, and the like. Of these diluents those of 3 to 4 carbon atoms per molecule are preferred, and isobutane is most preferred.
- DETD The rate of discharge of the polymerization effluent is such as to allow a continuous process stream from the slurry loop reactor from the point of discharge of the liquified polymerization effluent through a single point discharge valve and also through the first flash tank and the associated vapor recovery and solids recovery systems. The rate of discharge of the polymerization effluent is such as to maintain a constant pressure in the slurry reactor and to eliminate intermittent high pressure pulses associated

with a discharge of a portion of the reactor contents that occurs with settling legs on slurry reactors.

- DETD In the embodiment illustrated in FIG. 1, the polymerization is carried out in a loop reactor 1. It will be understood that while the loop reactor 1 is illustrated with four vertical legs, the loop reactor 1 may be equipped with more legs, desirably eight or more legs, desirable between 8 and 20, more desirable between 8 and 16, most desirable with 12 legs. The polymerization slurry is directionally circulated throughout the loop reactor 1 as illustrated by arrows A-D by one or more pumps, such as axial flow pumps, 2A and 2B. Desirably, the loop reactor 1 is equipped with multiple pumps wherein each pump is dedicated to an even number of legs, such as for example, four legs, six legs, eight legs, etc. Diluent comonomer and monomer are introduced into the loop reactor 1 from the diluent storage vessel 40, the comonomer storage vessel 41, and the monomer source 42 through their respective treater beds 37, 38, and 39 through conduits 5, 4 and 3, respectively, connected to conduit 6. Catalyst is added to the loop reactor 1 through one or more catalyst feed systems 7A and 7B. Normally, catalyst is introduced in a hydrocarbon diluent. DETD
- Polymerization slurry may be removed from the loop reactor by continuous discharge through a discharge conduit 8A. It will be understood that the loop reactor 1 may be equipped with one or more discharge conduits 8A. It will be also understood that the discharge conduit(s) 8A may be operated in a continuous or discontinuous mode, but desirably a continuous mode. The discharge conduit 8A extends for a distance through a portion of the wall of the loop reactor 1 and into the circulating polymerization slurry. By extending for a distance into the polymerization slurry, the discharge conduit 8A may remove polymerization effluent from the circulating polymerization slurry over an area defined from near or adjacent the inside wall of the loop reactor 1 to a distance extending into the circulating polymerization slurry. In this way, a higher weight percentage of polymer solids may be formed within the conduit 8A and ultimately removed from the loop reactor 1 than the weight percentage of polymer solids within the otherwise circulating polymerization slurry. A pressure control system (not shown in FIG. 1) operates in concert with the discharge conduit 8A. The discharge conduit 8A and the pressure control system 410 are more clearly illustrated in FIGS. 3 and 4 and will be discussed in greater detail below.
- DETD A pump 25 is provided for conveying the condensed liquid medium from the accumulator 24B back to the polymerization zone by a conduit 26. In this way, the unreacted/under-reacted catalyst and polymer solids not removed by the cyclone 13 are returned for further polymerization to the loop reactor 1.
- DETD Turning now to FIG. 3, a portion of a wall 310 of the loop reactor 1 through which the discharge conduit 8A extends is illustrated. The discharge conduit 8A may extend into the reactor at various angles. Desirably, the discharge conduit 8A extends into the loop reactor at substantially a right angle relative to the wall 310.
- DETD The wall 310 includes an inside surface 312 and an outside surface 314. The inside surface 312 supports the circulating polymerization slurry illustrated by directional arrows 318. The discharge conduit 8A has a top 316A, and a continuous side 316B. Portions of the side 316B define an opening 320. The opening 320 has a vertical opening

DETD

DETD

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dimensions v1 and v2 defined by walls 320A and 320B of the side 316B.
Desirably, the v1 dimension is greater than the v2 dimension. The
opening 320 has horizontal opening dimensions h1 and h2 (not shown). The
opening 320 may be formed in any suitable shape, such as rectangular,
oval, or a combination thereof. In one embodiment, the opening 320 may
be conical-shaped or scooped shaped.
The opening 320 communicates with a channel 322 defined by the inside
surfaces of the top 316A and the side 316B. The channel 322 conveys
captured polymerization slurry, illustrated by
directional arrow 324 to the discharge valve 8B (not shown).
The opening 320 is sized and positioned relative to the direction of
movement of the circulating polymerization slurry
318. Desirably, the opening 320 is in a substantially facing position to
the direction of the circulating polymerization slurry
318. More desirably, the opening 320 faces the direction of the
circulating slurry 318. In this way, a portion of the
polymerization slurry 324 containing polymer solids is
removed from the circulating polymerization slurry
318 over an area from near or adjacent the inside wall 312 of the
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loop reactor 1 to a distance extending into the circulating polymerization slurry 318. In this way, a higher weight percentage of polymer solids may be formed within the conduit 8A than the weight percentage of polymer solids within the otherwise circulating polymerization slurry.

DETD This weight percentage increase of polymer solids may depend upon the location of the discharge conduit 8A along the loop reactor 1, the insertion depth of the discharge conduit 8A within the loop reactor, the size and configuration of the opening 320, the orientation of the opening 320 relative to the direction of the circulating polymerization slurry, and the weight percentage of polymer solids in the circulating polymerization slurry 318. For example, between 1 to 5

weight percentage calculated increase is observed with a discharge conduit 8A having an v1 dimension of approximately 5 inches and a h1 dimension of approximately 1 inch. The discharge conduit 8A was positioned 10 ft downstream of a 90 degree bend in the loop reactor 1 in a portion of the loop reactor wall 314 adjacent the ground. The discharge conduit 8A extended approximately 5.5 inches into the circulating polymerization slurry stream. The velocity of the circulating polymerization slurry was in the range of 28 to 34 ft/sec with weight percent of polymer solids in the range of 48 to 5.

ft/sec with weight percent of polymer solids in the range of 48 to 53. Turning now to FIG. 5, another embodiment in accordance with the present DETD invention. In this embodiment, discharge conduit 8C extends through a portion, preferably a lower portion, of a wall 310 of the loop reactor 1. Wall 310 is part of the outside wall of the loop reactor (FIG. 7). As used herein, "outside wall" means that portion of the reactor wall towards which the solids in the loop reactor slurry tend to flow, by centrifugal force, when the slurry travels through a bend in the loop reactor. As shown in FIG. 7, the illustrated "outside wall" is the lower portion 310 of the reactor wall. At least a portion of the discharge conduit 8C is curved along its longitudinal axis inside the loop reactor. Without wishing to be bound by theory, it is believed that this avoids or substantially reduces turbulence of the circulating polymerization slurry flow once it enters the discharge conduit. The opening 325, preferably, located at the end of the curved conduit inside the loop reactor is substantially facing the flow of the circulating slurry 318. In a preferred embodiment in accordance with the present invention, the

- discharge conduit is located within a middle portion of the curved portion of the loop reactor, more preferably substantially at the middle of the curved portion, most preferably in a lower leg of the reactor.
- DETD In a preferred embodiment in accordance with the present invention, the curved portion 310 of the loop reactor comprises a 20 to 270 degree bend, preferably a 80 to 200 degree bend, more preferably a 90 to 180 degree bend, and most preferably a 180 degree bend.
- DETD In another preferred embodiment, the discharge conduit 8C is located substantially at the bottom of a 180 degree bend of the loop reactor 1. Such an embodiment is illustrated schematically in FIG. 6. In this embodiment at least one bottom leg 328 of the reactor has a bend of about 180 degrees. In other words, instead of being a substantially straight section located between two 90 degree bends, the lower leg of the loop reactor is substantially "U" shaped. In this embodiment, discharge conduit 8C is preferably located substantially in a central portion of generally U shaped bottom leg 328 and extends through the bottom wall 310 of the reactor 1. In this embodiment, the opening 325 is located inside the loop reactor in any position but preferably close to the outside wall in the lower leg of the loop reactor so as to capture a higher concentration of solids than the average concentration of solids in the loop reactor. Without wishing to be bound by the theory, it is believed that the centrifugal force of the circulating flow cause a higher concentration of solids in the lower portion of the cross-section of the lower leg. For example, in one embodiment, the average concentration of solids in the loop reactor is about 55 wt. % and the captured solids concentration is above 57 wt. %, preferably above 60 wt. %, more preferably above 65 wt. %. In one embodiment as illustrated schematically in FIG. 7, the opening 325 is located closer to the outside wall 310 of the loop reactor than to the inside wall 330 of the loop reactor. Preferably, the opening is located closer to the outside wall 310 of the loop reactor than to the center 331 of the loop reactor. More preferably, the opening is closely adjacent to the outside wall of the loop reactor. Most preferably, the opening touches the outside wall of the loop reactor.
- DETD In yet another preferred embodiment, the section of the discharge conduit 8C inside the loop reactor is bent in a curve towards the flow of the slurry 318 of the loop reactor. The discharge conduit has a diameter less than that of the loop reactor legs to avoid interference with the flow of the polymerization slurry circulation inside the loop reactor. Preferably, the discharge conduit has a diameter 5-40% of the diameter of loop reactor, more preferably 7-25%, and most preferably 8-15%. The diameter of the loop reactor is measured in the immediate area of the opening of the discharge conduit. In one example, the discharge conduit is a pipe having a substantially circular transverse cross section of about 2-inch diameter which the diameter of the loop reactor in the immediate area is about 20 inches.
- DETD In another embodiment, the discharge conduit 8C is curved substantially towards the flow of the circulating slurry. Preferably, the curve is from about 45 degrees to about 135 degrees. More preferably, the curve is from about 75 degrees to about 135 degrees. In one embodiment, as illustrated schematically in FIG. 5, the face of the opening at the end

of the discharge conduit defines a plane 329 which intersects an outside wall of the loop reactor at a tangent line which is substantially perpendicular to the plane.

- Turning now to FIG. 4, the pressure control system 410 is illustrated. The pressure control system 410 operates to maintain substantially uniform pressure within the loop reactor 1 by controlling the discharge of polymerization effluent from the loop reactor 1 via the discharge conduit 8A. The control system 410 also operates to prevent plugging of the discharge conduit 8A by polymer solids during pressure fluctuations within the loop reactor 1 and/or when the flow of polymerization effluent from the discharge conduit 8A to conduit 9 is interrupted and/or stopped.
- DETD The pressure control system 410 includes a first inert diluent source 412, such as isobutane, and an inert diluent conduit 414 in communication with a loop reactor conduit 416. The flow of inert diluent through the inert diluent conduit 414 to the loop reactor conduit 416 is controlled by the control valve 418 in concert with a flow element 420 and a flow indicator controller 422. The purpose of metering the flow of inert diluent from the first inert diluent source 412 to the loop reactor 1 is to prevent plugging of the conduit 416 by polymer solids. In this way, a loop reactor pressure element 441 (discussed below), in communication with the loop reactor conduit 416, may more accurately monitor the pressure in the loop reactor 1.
- DETD The pressure control system 410 further includes as second inert diluent source 424 and a third inert diluent source 426. Inert diluent, such as isobutane, from the second inert diluent source 424 flows into a conduit 428 towards a control valve 430 which is in fluid communication with a conduit 432. The control valve 430, in concert with a flow element 431 and a flow indicator controller 433, meters the flow of inert diluent from the second inert diluent source 424 into conduit 432. The conduit 432 is in fluid communication with a conduit 434 and the discharge conduit 8A, terminating in the discharge conduit 8A at a point between the loop reactor 1 and the discharge valve 8B. The purpose of metering the flow of inert diluent from the second inert diluent source 422 into the conduit 432 is to prevent plugging of the conduit 432 by polymer solids which might otherwise back flow into the conduit 432 from the discharge conduit 8A. Additionally, the flow of inert diluent from the second inert diluent source 422 also prevents plugging of the conduit 434 and the control valve 440 by polymer solids which might back flow into conduit 432 from the discharge conduit 8A. Inert diluent from the third inert diluent source 426 flows into a DETD conduit 438 towards a control valve 440 which is in fluid communication
- conduit 438 towards a control valve 440 which is in fluid communication with conduit 434. As will be explained in greater detail below, in the event of a sufficient pressure fluctuation within the loop reactor 1, the control valve 440 operates to initiate a sufficient flow under sufficient pressure of inert diluent from the third inert diluent source 426 to purge and/or discharge polymer solids from the discharge conduit 8A into the loop reactor

 1. In this instance, generally the flow of inert diluent from the third inert diluent source 426 into the conduit 432 will be greater than the flow of inert diluent from the second inert diluent source 424 into the conduit 432. For example, the flow of inert diluent from the second inert diluent source 424 to the discharge conduit 8A may be in a range of 0.5 to less than 2.0 gallons/min. The flow of inert diluent from the third inert diluent source 426 to the discharge conduit 8A may be in a range of 2.0 to 20 gallons/min.
- DETD The loop reactor pressure element 441 and a pressure

indicating controller 442 perform several functions. As previously mentioned, the pressure element 441 monitors the loop reactor 1 pressure via the conduit 416. In response to this pressure, the loop reactor pressure element 441 generates an signal proportional to the pressure in conduit 416. This signal is conveyed to the pressure indicating controller 442. In response to this signal and a preset pressure value, the pressure indicating controller 442 sends a signal through a signal conduit (illustrated by the broken line 444) to the discharge valve 8B and the control valve 440.

DETD During normal loop reactor operations, the discharge valve 8B is positioned to permit the flow of polymerization effluent from the discharge conduit 8A to conduit 9. At the same time, the control valve 440 is closed preventing the flow of inert diluent from the third inert diluent source 426 to the discharge conduit. When sufficient pressure fluctuations occur and/or when partial depressurization in the loop reactor 1 are detected by the loop reactor pressure element 441, the signal generated by the pressure indicating controller 442 causes the discharge valve 8B to close and the control valve 440 to open. By closing discharge valve 8B, thus interrupting the discharge from the loop reactor 1, pressure within the loop reactor 1 may be restored. By opening the control valve 440 and flowing sufficient volumes of inert diluent from the third inert diluent source 426 into the discharge conduit 8A under sufficient pressure, polymer solids remaining in the discharge conduit 8A between the discharge valve 8B and the loop reactor 1 may be flushed out of and/or purged from the discharge conduit 8A and into the loop reactor 1. Additionally, by maintaining a sufficient flow of inert diluent, continuous or otherwise, into and/or through the discharge conduit 8A while the discharge valve 8B is closed, the polymer solids within the loop reactor 1 are prevented from entering and/or substantially collecting in the discharge conduit 8A and/or plugging the discharge conduit 8A. Upon return of normal operations, the control valve 440 closes terminating the flow of inert diluent from the third inert diluent source 426 and the discharge valve 8B opens to resume the flow of polymerization effluent through the discharge conduit 8A into the conduit 9.

DETD

TABLE 1

EXAMPLE 3 EXAMPLE 4

ETHYLENE POLYMERIZATION DATA

	Difference of	1 11111111
Nominal pump(s) size, inches	20	20
Reactor solids concentration, wt. %	46-48	54-57
Polymer production rate, K lbs./hr.	28-31	38-42
Reactor circulation pump power, KW	460-480	890-920
Circulation pump head, ft.	85-110	190-240
Circulation rate, GPM	21,000-28,000	23,000-30,000
Reactor slurry density, gm/cc	0.555-0.565	0.588-0.592
Reactor temperature, degrees F	215-218	217-218
Ethylene concentration, wt. %	4.0 - 4.4	
5.0-6.0		
Hexene concentration, wt. %	0.13-0.19	0.13 - 0.19
Heat transfer coefficient, btu/hr-f-ft	215-225	230-245
Reactor volume, gallons	11,500	11,500
Reactor length, ft.	833	833
Circulating pump head		
per reactor length, ft/ft	0.100-0.132	0.228-0.288

Catalyst productivity, 1b/1b 2,700-3,000 2,700-3,000 Polymer residence time, hrs. 0.83-0.92 0.68-0.79 Space time yield, 1bs/hr-gal 2.4-2.7 3.3-3.7 Isobutane compressed and recycled, % 100 45-60

It has been observed that by increasing the head and flow capability of DETD the loop reactor circulating pump(s), higher weight percent solids can be circulated in the reactor. It has also been observed that attaining the necessary head and flow from one pump is increasingly difficult as percent solids are increased above 45 weight percent and/or reactor length is increased. Therefore, the use of two pumps in series allows a doubling of pumping head capability and a resulting percent solids increase. Increased weight percent solids in the loop reactor increases catalyst residence time, which for chrome oxide and Ziegler-Natta catalysts, increases catalyst productivity. One can choose to take advantage of higher percent solids and longer residence time by keeping production rate constant at reduced catalyst feed rate and improve the catalyst yield. Another alternative is to maintain catalyst feed rate constant and increase the reactor throughput and therefor increase STY at nearly constant catalyst productivity. Higher solids also increases the weight percent solids removed from the reactor which reduces isobutane processing cost in recycle equipment. Desirably, the higher solids are removed continuously. Continuous discharge may occur through a single point discharge line.

DETD In a loop reactor, it is not always possible to locate the continuous discharge line in an optimal location to take advantage of centrifugal force to increase the weight percent solids and therefore reduce the amount of isobutane entrained with the polymer solids. It has been observed that a specifically designed pipe as illustrated in FIG. 3 inserted into the loop reactor can increase weight percent solids removed from the reactor. This pipe insert will function in any section of the loop reactor and in a straight section will increase the weight percent solids to that equal to that in a location which takes advantage of centrifugal force to concentrate solids.

DETD With the development of high weight percent solids circulation capability in the loop reactor and two-stage flash, the need to concentrate solids in the reactor discharge is reduced compared to the conventional loop reactor operations having low solids circulation, single-stage flash, continuous discharge line, and continuous discharge or otherwise. Therefore, the conventional loop reactor settling legs, which are designed to maximize polymer solids concentration prior to discharge, can be replaced with a continuous discharge line, which simplifies the system mechanically, reduces capital cost, improves safety, reduces maintenance and improves reactor control. Settling legs require routine maintenance due to their plugging tendency and can form material which plugs downstream polymer handling equipment. Maximum loop reactor ethylene concentration is limited by settling legs due to the tendency for polymer to grow in the legs at elevated ethylene concentrations between discharges and therefore plug the leg. Continuous discharge eliminates this tendency. Another advantage of continuous discharge is better response to a sudden drop in reactor pressure, which can happen if ethylene flow is quickly reduced. Under this condition, settling legs will stop discharging and can plug with polymer within minutes

DETD The condenser provides for low variable and capital cost liquefaction of the diluent removed from the rector with the polymer via the first flash tank. Conventional single flash tank systems flash the polymerization

effluent to the just above ambient pressure, which requires compression to liquefy the diluent prior to recycle to the loop reactor. An intermediate pressure flash provides for condensation with a commonly available cooling medium, such as Plant cooling water. The condenser system is flushed with diluent and designed to accommodate a level of fines without accumulation or plugging. The condenser is cooled by a tempered water system which controls the condensation temperature to achieve the proper vapor pressure in the accumulator to allow efficient pressure control by the pressure control valve on the accumulator vent. The condenser tempered water system is a pump-around loop of cooling water, the temperature of which is controlled by metering in fresh cooling water as needed.

- DETD The accumulator receives the condensed diluent and catalyst/polymer fines and pumps the mixture back to the loop reactor based on level control in the accumulator. The accumulator has a bottom shape designed to accommodate fines. A vent on the accumulator purges the accumulated diluent of light-ends/non-condensables and controls pressure on the first flash system.
- DETD The second flash tank, operating just above ambient pressure, receives polymer from the first flash tank seal chamber. Complete vaporization, if not already accomplished in the first flash tank, will occur in the second flash tank. Polymer leaves the bottom of the second flash tank to the dryer system. The flash-line heater would increase the temperature of the polymer which allows the dryer system to remove residual volatiles more efficiently and effectively. The overhead of the second flash tank will be diluent vapor not recovered in the first flash system and will be filtered and compressed for return to the loop reactor.
- CLM What is claimed is:
 - 1. A slurry loop reactor containing a flow of slurry therein, comprising: a discharge conduit extending a distance into the loop reactor; the conduit having a longitudinal axis and an opening inside the loop reactor; at least a portion of the conduit being curved along its longitudinal axis; and the opening substantially facing the flow of the slurry; the discharge conduit being located substantially at the middle of a curved portion of the loop reactor; the curved portion of the loop reactor comprising a lower leg of the loop reactor; the curved portion of the loop reactor comprising a 180 degree bend; the discharge conduit being curved along its longitudinal axis more than about 75 degrees but less than about 135 degrees; the face of the opening defining a plane which intersects an outside wall of the loop reactor at a tangent line being substantially perpendicular to the plane; the discharge conduit having a diameter which is about 8-15% of the inside diameter of the loop reactor; and the opening is closer to the outside half wall than the center line of the loop reactor.
- CLM What is claimed is:
 - 2. A slurry loop reactor containing a flow of slurry therein, comprising: a discharge conduit extending a distance into the loop reactor; the conduit having a longitudinal axis and an opening inside the loop reactor; at least a portion of the conduit being curved along its longitudinal axis inside the loop reactor; and the opening substantially facing the flow of the slurry, wherein the discharge conduit is located within a lower leg of the loop reactor.
- CLM What is claimed is:

- 3. The loop reactor according to claim 2, wherein the discharge conduit is located within a curved portion of the loop reactor.
- CLM What is claimed is:
 4. The loop reactor according to claim 3, wherein
 the discharge conduit is located within a middle portion of the curved
 portion of the loop reactor.
- CLM What is claimed is:
 5. The loop reactor according to claim 4, wherein the discharge conduit is located substantially at the middle of the curved portion of the loop reactor.
- CLM What is claimed is:
 6. The loop reactor according to claim 4, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is
 substantially perpendicular to the plane.
- CLM What is claimed is:
 7. The loop reactor according to claim 4, wherein the discharge conduit has a diameter which is about 5-40% of the inside diameter of the loop reactor.
- CLM What is claimed is:
 8. The loop reactor according to claim 4, wherein the discharge conduit has a diameter which is about 7-25% of the inside diameter of the loop reactor.
- CLM What is claimed is:

 9. The loop reactor according to claim 4, wherein the discharge conduit has a diameter which is about 8-15% of the inside diameter of the loop reactor.
- CLM What is claimed is:
 10. The loop reactor according to claim 3, wherein
 the discharge conduit is located substantially at the middle of the
 curved portion of the loop reactor.
- CLM What is claimed is:
 11. The loop reactor according to claim 10, wherein the curved portion comprises a 20 to 270 degree bend.
- CLM What is claimed is:
 12. The loop reactor according to claim 10, wherein the curved portion comprises a 80 to 200 degree bend.
- CLM What is claimed is:
 13. The loop reactor according to claim 10, wherein the curved portion comprises a 90 to 180 degree bend.
- CLM What is claimed is:
 14. The loop reactor according to claim 10, wherein the curved portion comprises a 180 degree bend.
- CLM What is claimed is:
 15. The loop reactor according to claim 10, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is

substantially perpendicular to the plane.

- CLM What is claimed is:
 16. The loop reactor according to claim 10, wherein
 the discharge conduit has a diameter which is about 5-40% of the inside
 diameter of the loop reactor.
- CLM What is claimed is: 17. The loop reactor according to claim 10, wherein the discharge conduit has a diameter which is about 7-25% of the inside diameter of the loop reactor.
- CLM What is claimed is:
 18. The loop reactor according to claim 10, wherein
 the discharge conduit has a diameter which is about 8-15% of the inside
 diameter of the loop reactor.
- CLM What is claimed is:
 19. The loop reactor according to claim 3, wherein the curved portion comprises a 20 to 270 degree bend.
- CLM What is claimed is:
 20. The loop reactor according to claim 19, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is
 substantially perpendicular to the plane.
- CLM What is claimed is:
 21. The loop reactor according to claim 3, wherein the curved portion comprises a 80 to 200 degree bend.
- CLM What is claimed is:
 22. The loop reactor according to claim 21, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is
 substantially perpendicular to the plane.
- CLM What is claimed is:
 23. The loop reactor according to claim 3, wherein the curved portion comprises a 90 to 180 degree bend.
- CLM What is claimed is:
 24. The loop reactor according to claim 3, wherein the curved portion comprises a 180 degree bend.
- CLM What is claimed is:
 25. The loop reactor according to claim 24, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is
 substantially perpendicular to the plane.
- CLM What is claimed is:
 26. The loop reactor according to claim 3, wherein
 the discharge conduit is curved along its longitudinal axis from about
 45 degrees to about 135 degrees.
- CLM What is claimed is:
 27. The loop reactor according to claim 3, wherein
 the discharge conduit is curved along its longitudinal axis from about
 75 degrees to about 135 degrees.

- CLM What is claimed is:
 - 28. The loop reactor according to claim 3, wherein the face of the opening defines a plane which intersects an outside wall of the loop reactor at a tangent line which is substantially perpendicular to the plane.
- CLM What is claimed is:
 29. The loop reactor according to claim 3, wherein

diameter of the loop reactor.

the discharge conduit has a diameter which is about 5-40% of the inside diameter of the loop reactor.

- CLM What is claimed is:
 - 30. The loop reactor according to claim 3, wherein the discharge conduit has a diameter which is about 7-25% of the inside diameter of the loop reactor.
- CLM What is claimed is:
 31. The loop reactor according to claim 3, wherein
 the discharge conduit has a diameter which is about 8-15% of the inside
- CLM What is claimed is:
 32. The loop reactor according to claim 2, wherein
 the discharge conduit is curved along its longitudinal axis from about
 45 degrees to about 135 degrees.
- CLM What is claimed is:

 33. The loop reactor according to claim 2, wherein the discharge conduit is curved along its longitudinal axis from about 75 degrees to about 135 degrees.
- CLM What is claimed is:

 34. The loop reactor according to claim 2, wherein
 the face of the opening defines a plane which intersects an outside wall
 of the loop reactor at a tangent line which is
 substantially perpendicular to the plane.
- CLM What is claimed is:
 35. The loop reactor according to claim 2, wherein the discharge conduit has a diameter which is about 5-40% of the inside diameter of the loop reactor.
- CLM What is claimed is:
 36. The loop reactor according to claim 2, wherein
 the discharge conduit has a diameter which is about 7-25% of the inside
 diameter of the loop reactor.
- CLM What is claimed is: 37. The loop reactor according to claim 2, wherein the discharge conduit has a diameter which is about 8-15% of the inside diameter of the loop reactor.
- CLM What is claimed is:

 38. The loop reactor according to claim 2, wherein the opening is located inside the loop reactor at a point where the concentration of solids of the slurry is higher than the average concentration of solids in slurry in the loop reactor.

CLM What is claimed is:
39. The loop reactor according to claim 38, wherein the opening is located closer to the outside wall of the loop reactor than to the inside wall of the loop reactor.

CLM What is claimed is:
40. The loop reactor according to claim 39, wherein the opening is located closer to an outside wall of the loop reactor than to the center of the loop reactor

CLM What is claimed is:
41. The loop reactor according to claim 40, wherein the opening is closely adjacent to the outside wall of the loop reactor.

CLM What is claimed is:
42. The loop reactor according to claim 41, wherein the opening touches the outside wall of the loop reactor.

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TI Producing bimodal polyethylene resins for pipes and films

IN Marechal, Philippe

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PΑ
     ATOFINA Research SA, Belg.
SO
     Eur. Pat. Appl., 18 pp.
      CODEN: EPXXDW
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      ICS C08F297-08; C08F002-00
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CLASS
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                        [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*];
                        C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02
                 NCL
                        526/064.000; 526/065.000; 526/124.200; 526/160.000;
                        526/348.400; 526/348.600
                 ECLA
                        C08F010/02+2/00B; B01J019/18C8
 US 20060189768
                 IPCI
                        C08G0085-00 [I,A]
                 NCL
                        526/065.000
                        B01J019/18C8; C08F010/02+2/00B
                 ECLA
AB
     A process for producing bimodal polyethylene resins, in 2 reactors in
     series, comprises producing a first polyethylene resin fraction in a first
     slurry loop reactor in a diluent in the presence of a catalyst and
     producing a second polyethylene resin fraction in a second slurry loop
     reactor in diluent in the presence of the catalyst, where the first
     polyethylene resin fraction is passed from the first reactor to the second
     reactor together with the catalyst, 1 of the reactors producing a resin
     fraction of higher mol. than the other, and characterized in that the
     first reactor is fed with ethylene and diluent having an ethylene content
     \geq70% based on the weight of the diluent and in that in the first
     reactor the slurry of polyethylene in the diluent has a solids content
     \geq 30\% based on the weight of the diluent. A relatively low mol. weight
     polyethylene is produced in the second reactor. When the first reactor
     high mol. weight product has a d. lower than that of the second reactor
     product, a material is made with slow crack growth resistance, determined by
     the notched pipe test.
ST
     polyethylene bimodal manuf dual reactor; impact strength improved
     polyethylene bimodal; pipe film polyethylene bimodal
ΙT
     Polymerization catalysts
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(Ziegler-Natta; producing bimodal polyethylene resins)
ΙT
     Polymerization catalysts
        (metallocene; producing bimodal polyethylene resins)
ΙT
     Polymer blends
     RL: TEM (Technical or engineered material use); USES (Uses)
        (polyethylenes; producing bimodal polyethylene resins)
ΙT
     Impact-resistant materials
        (producing bimodal polyethylene resins)
ΙT
     Pipes and Tubes
        (producing bimodal polyethylene resins for)
ΙT
     Polymerization
        (slurry, in slurry loop reactor; producing bimodal polyethylene resins)
ΙT
     9002-88-4P, Polyethylene 25213-02-9P, Ethylene-1-hexene copolymer
     RL: IMF (Industrial manufacture); TEM (Technical or engineered material
     use); PREP (Preparation); USES (Uses)
        (producing bimodal polyethylene resins)
             THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE.CNT
(1) Fina Research; EP 0580930 A 1994 CAPLUS
(2) Fina Research; EP 0649860 A 1995 CAPLUS
(3) Fina Research; EP 0832905 A 1998 CAPLUS
(4) Neste, O; WO 9212181 A 1992 CAPLUS
(5) Scheirs, J; TRENDS IN POLYMER SCIENCE 1996, V4(12) CAPLUS
(6) Solvay; EP 0897934 A 1999 CAPLUS
L8
      ANSWER 2 OF 2
                          INPADOCDB COPYRIGHT 2008 EPO/FIZ KA on STN
      49389877 INPADOCDB
ΑN
      3888164
FN
ΤI
      Process for producing bimodal polyethylene resins.
TI.
      English
     MARECHAL PHILIPPE
ΙN
INS
     MARECHAL PHILIPPE, BE
PA
      TOTAL PETROCHEMICALS RESEARCH FELUY
PAS
      TOTAL PETROCHEMICALS RES FELUY, BE
DT
      Patent
PΙ
      US 7034092
                          B2 20060425 English
      USB2 REEXAM. CERTIF., N-ND REEXAM. or GRANTED PATENT AS SECOND
      PUBLICATION [FROM 2001 ONWARDS]
DAV
      20060425 printed-with-grant
STA
      GRANTED
ΑI
     US 2003-398162
                           A 20031117
     USA Patent application
AIT
PRAI EP 2000-121646
                              20001004
                                        (EPA, 20070802)
                          А
                              20011002
     WO 2001-EP11394
                           W
                                        (WOWW)
PRAIT EPA Patent application
      WOWW Additional PCT application
      10. THERE ARE 10 CITED REFERENCES (10 PATENT, 0 NON PATENT) AVAILABLE FOR
REC
      THIS RECORD. ALL CITATIONS ARE AVAILABLE IN THE RE FORMAT.
     C08F0002-14
                      [I,A]; C08F0210-02
                                             [I,A]; C08F0002-12
                                                                       [I,C*];
      C08F0210-00
                      [I,C*]
                      [I,A]; C08F0002-00
                                              [I,A]; C08F0010-02
IPCR B01J0019-18
                                                                       [I,A]
                      [I,C*]; C08F0002-00
      B01J0019-18
                                              [I,C*]; C08F0010-00
                                                                       [I,C*]
      X5263484; X526 64; X526160; 526 65; X5263486; X5261242
NCL
EPC
     B01J0019-18C8; C08F0010-02+2/00B
ICO
      L01J0219:00A6L
AΒ
      A process for producing bimodal polyethylene resins in two reactors in
      series, the process comprising producing a first polyethylene resin
      fraction in a first slurry loop reactor in a diluent in the presence of a
      catalyst and producing a second polyethylene resin fraction in a second
```

slurry loop reactor, serially connected to the first reactor, in the diluent in the presence of the catalyst, the first polyethylene resin fraction being passed from the first reactor to the second reactor together with the catalyst, one of the first and second reactors producing a resin fraction of higher molecular than the resin fraction produced by the other of the first and second reactors, characterised in that the first reactor is fed with a feed of ethylene and diluent having an ethylene content of at least 70 wt % based on the weight of the diluent and in that in the first reactor the slurry of polyethylene in the diluent has a solids content of at least 30 wt % based on the weight of the diluent.

-0.80

-0.80

AL English

AS national office

CA SUBSCRIBER PRICE

FA AB; AI; AN; DAV; DT; EPC; ICO; IN; INS; IPC; IPCI; IPCR; LA; NCL; PA; PAS; PI; PIT; PRAI; REP; TI

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ENTRY SESSION

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=> s wo 2002028922/pn L9 2 WO 2002028922/PN

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L9 ANSWER 1 OF 2 INPADOCDB COPYRIGHT 2008 EPO/FIZ KA on STN

AN 14657453 INPADOCDB UP 20070315 UW 200711

FN 3888164

TI PROCESS FOR PRODUCING BIMODAL POLYETHYLENE RESINS.

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PROCEDE DESTINE A LA PRODUCTION DE RESINES DE POLYETHYLENE BIMODALES.
      English; French
TL
TN
      MARECHAL, PHILIPPE
INS
     MARECHAL PHILIPPE, BE
      ATOFINA RESEARCH; MARECHAL, PHILIPPE
PA
PAS
      ATOFINA RES, BE; MARECHAL PHILIPPE, BE
DT
      Patent
PΙ
      WO 2002028922
                          A1 20020411
PIT
      WOA1 INTERNATIONAL PUBLICATION WITH INTERNATIONAL SEARCH REPORT
FDT
      W0100000 With international search report;
      W0030000 Before expiration of time limit for amending the claims and to
      be republished in the event of the receipt of the amendments
DAV
      20020411 examined-printed-without-grant
STA
      PRE-GRANT PUBLICATION
DS
                    AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ
                    DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP
                    KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ
                    NO NZ PH PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG
                    US UZ VN YU ZA ZW
      RW (ARIPO):
                    GH GM KE LS MW MZ SD SL SZ TZ UG ZW
      RW (EAPO):
                   AM AZ BY KG KZ MD RU TJ TM
      RW (EPO):
                    AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR
      RW (OAPI):
                    BF BJ CF CG CI CM GA GN GO GW ML MR NE SN TD TG
                             20011002 English
      WO 2001-EP11394
ΑI
                          W
     WOW International application Number
AIT
PRAI EP 2000-121646
                          A 20001004 (EPA, 20070802)
PRAIT EPA Patent application
      7. THERE ARE 7 CITED REFERENCES (6 PATENT, 1 NON PATENT) AVAILABLE FOR
      THIS RECORD. ALL CITATIONS ARE AVAILABLE IN THE RE FORMAT.
IC.V
ICM
     C08F010-02
      C08F297-08; C08F002-00; C08F002-14
ICS
IPCR B01J0019-18
                      [I,A]; C08F0002-00
                                              [I,A]; C08F0002-14
                                                                      [I,A];
     C08F0010-02
                      [I,A]
                      [I,C*]; C08F0002-00
                                             [I,C*]; C08F0002-12
     B01J0019-18
                                                                      [I,C*];
     C08F0010-00
                      [I,C*]
EPC
     B01J0019-18C8; C08F0010-02+2/00B
ICO
     L01J0219:00A6L
AΒ
      A process for producing bimodal polyethylene resins in two reactors in
      series, the process comprising producing a first polyethylene resin
      fraction in a first slurry loop reactor in a diluent in the presence of a
      catalyst and producing a second polyethylene resin fraction in a second
      slurry loop reactor, serially connected to the first reactor, in the
      diluent in the presence of the catalyst, the first polyethylene resin
      fraction being passed from the first reactor to the second reactor
      together with the catalyst, one of the first and second reactors
      producing a resin fraction of higher molecular than the resin fraction
      produced by the other of the first and second reactors, characterised in
      that the first reactor is fed with a feed of ethylene and diluent having
      an ethylene content of at least 70 wt% based on the weight of the diluent
      and in that in the first reactor the slurry of polyethylene in the
      diluent has a solids content of at least 30 wt% based on the weight of
      the diluent.
      English
AL
      national office
     La presente invention concerne un procede vidant a la production de
      resines de polyethylene bimodales dans deux reacteurs en serie. A cet
      effet, on produit une premiere fraction de resine de polyethylene dans un
      premier reacteur en boucle a combustible en suspension dans un diluant en
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presence d'un catalyseur. On produit ensuite une seconde fraction de

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resine de polyethylene dans un second reacteur en boucle a combustible en suspension dans un diluant en presence d'un catalyseur. Ce second reacteur est monte en serie avec le premier reacteur, la premiere fraction de resine de polyethylene passant du premier reacteur au second reacteur en meme temps que le catalyseur. L'un de ces deux reacteurs produit une fraction de resine de masse moleculaire superieure a celle de l'autre des deux reacteurs. Le procede est caracterise en ce que le premier reacteur est alimente en ethylene et diluant dont la teneur en ethylene est d'au moins 70% en masse par rapport a la masse de diluent, et que dans le premier reacteur, la suspension de polyethylene dans le diluant presente une teneur en corps solides d'au moins 30% en masse par rapport a la masse du diluant. French national office AB; ABFR; AI; AN; DAV; DS; DT; EPC; ICM; ICO; ICS; IN; INS; IPC; IPCR; LAF; PA; PAS; PI; PIT; PRAI; REN; REP; REXP; TI CHG CIT A ANSWER 2 OF 2 CAPLUS COPYRIGHT 2008 ACS on STN 2002:272835 CAPLUS 136:295236 Entered STN: 12 Apr 2002 Producing bimodal polyethylene resins for pipes and films Marechal, Philippe ATOFINA Research SA, Belg. Eur. Pat. Appl., 18 pp. CODEN: EPXXDW Patent English ICM C08F010-02 ICS C08F297-08; C08F002-00 35-4 (Chemistry of Synthetic High Polymers) FAN.CNT 1 PATENT NO. KIND DATE APPLICATION NO. DATE ____ _____ _____ A1 20020410 EP 2000-121646 20001004 EP 1195388 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO WO 2001-EP11394 WO 2002028922 A1 20020411 W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG AU 2002021642 Α 20020415 AU 2002-21642 20011002 EP 1322681 Α1 20030702 EP 2001-986305 20011002 AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR JP 2004514743 Τ 20040520 JP 2002-532503 20011002 NO 2003001432 NO 2003-1432 Α 20030328 20030328 В1 KR 803995 20080218 KR 2003-704765 20030403 A1 US 20040077803 20040422 US 2003-398162 20031117 A1 20040422 B2 20060425 US 7034092 US 20060189768 A1 20060824
PRAI EP 2000-121646 A 20001004
WO 2001-EP11394 W 20011002 US 2006-410169 20060424

US 2003-398	162	A1 20031117
CLASS PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
EP 1195388	ICM ICS IPCI	C08F010-02 C08F297-08; C08F002-00 C08F0010-02 [ICM,6]; C08F0010-00 [ICM,6,C*]; C08F0297-08 [ICS,6]; C08F0297-00 [ICS,6,C*]; C08F0002-00 [ICS,6]
IPCR	C08F0002-00 [ICS, 6] B01J0019-18 [I,C*]; B01J0019-18 [I,A]; C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02 [I,A]	
ECLA	B01J019/18C8; C08F010/02+2/00B	
WO 2002028922 IPCI IPCR	IPCI	C08F0010-02 [ICM,7]; C08F0010-00 [ICM,7,C*]; C08F0297-08 [ICS,7]; C08F0297-00 [ICS,7,C*]; C08F0002-00 [ICS,7]; C08F0002-14 [ICS,7]; C08
	B01J0019-18 [I,C*]; B01J0019-18 [I,A]; C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02	
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	[ICS,7,C*] B01J0019-18 [I,C*]; B01J0019-18 [I,A]; C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02	
ECLA IPCI IPCR	[I,A] B01J019/18C8; C08F010/02+2/00B C08F0010-02 [ICM,7]; C08F0010-00 [ICM,7,C*]; C08F0297-08 [ICS,7]; C08F0297-00 [ICS,7,C*]; C08F0002-00 [ICS,7]; C08F0002-14 [ICS,7]; C08F0002-	
	[ICS,7,C*] C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02 [I,A]; C08F0297-00 [I,C*]; C08F0297-08	
JP 2004514743 IPCI IPCR FTERM	[I,A] C08F0010-02 [ICM,7]; C08F0010-00 [ICM,7,C*] C08F0010-00 [I,C*]; C08F0010-02 [I,A] 4J100/AA02P; 4J100/AA04Q; 4J100/AA16Q; 4J100/AA19Q	
No. 20022011422	TDOT	4J100/CA01; 4J100/CA04; 4J100/DA06; 4J100/FA09; 4J100/FA10; 4J100/FA19; 4J100/FA37; 4J100/FA41; 4J100/FA47
NO 2003001432	IPCI IPCR	C08F [ICM, 7] B01J0019-18 [I,C*]; B01J0019-18 [I,A]; C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02 [I,A]
KR 803995 IPCI US 20040077803 IPCR	IPCI	B01J019/18C8; C08F010/02+2/00B C08F0010-02 [I,A]; C08F0010-00 [I,C*] C08F0002-14 [I,A]; C08F0002-12 [I,C*]; C08F0210-02 [I,A]; C08F0210-00 [I,C*]
	B01J0019-18 [I,C*]; B01J0019-18 [I,A]; C08F0002-00 [I,C*]; C08F0002-00 [I,A]; C08F0002-12 [I,C*]; C08F0002-14 [I,A]; C08F0010-00 [I,C*]; C08F0010-02	
	NCL	[I,A] 526/064.000; 526/065.000; 526/124.200; 526/160.000;

526/348.400; 526/348.600

ECLA C08F010/02+2/00B; B01J019/18C8

US 20060189768 IPCI C08G0085-00 [I,A]

NCL 526/065.000

ECLA B01J019/18C8; C08F010/02+2/00B

AΒ A process for producing bimodal polyethylene resins, in 2 reactors in series, comprises producing a first polyethylene resin fraction in a first slurry loop reactor in a diluent in the presence of a catalyst and producing a second polyethylene resin fraction in a second slurry loop reactor in diluent in the presence of the catalyst, where the first polyethylene resin fraction is passed from the first reactor to the second reactor together with the catalyst, 1 of the reactors producing a resin fraction of higher mol. than the other, and characterized in that the first reactor is fed with ethylene and diluent having an ethylene content \geq 70% based on the weight of the diluent and in that in the first reactor the slurry of polyethylene in the diluent has a solids content ≥30% based on the weight of the diluent. A relatively low mol. weight polyethylene is produced in the second reactor. When the first reactor high mol. weight product has a d. lower than that of the second reactor product, a material is made with slow crack growth resistance, determined by the notched pipe test.

ST polyethylene bimodal manuf dual reactor; impact strength improved polyethylene bimodal; pipe film polyethylene bimodal

IT Polymerization catalysts

(Ziegler-Natta; producing bimodal polyethylene resins)

IT Polymerization catalysts

(metallocene; producing bimodal polyethylene resins)

IT Polymer blends

RL: TEM (Technical or engineered material use); USES (Uses)

(polyethylenes; producing bimodal polyethylene resins)

IT Impact-resistant materials

(producing bimodal polyethylene resins)

IT Pipes and Tubes

(producing bimodal polyethylene resins for)

IT Polymerization

(slurry, in slurry loop reactor; producing bimodal polyethylene resins)

9002-88-4P, Polyethylene 25213-02-9P, Ethylene-1-hexene copolymer RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(producing bimodal polyethylene resins)

RE.CNT 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD RE

- (1) Fina Research; EP 0580930 A 1994 CAPLUS
- (2) Fina Research; EP 0649860 A 1995 CAPLUS
- (3) Fina Research; EP 0832905 A 1998 CAPLUS
- (4) Neste, O; WO 9212181 A 1992 CAPLUS
- (5) Scheirs, J; TRENDS IN POLYMER SCIENCE 1996, V4(12) CAPLUS
- (6) Solvay; EP 0897934 A 1999 CAPLUS

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